UNIVERSITY OF MINNESOTA
RECEIVED
OCT 13 1960
CHEMISTRY LIBRARY

# Journal

of the

# Indian Chemical Society

July, 1960

1960 Vol. XXXVII No. 7

Published by the Indian Chemical Society
92, Acharya Prafulla Chandra Road, Calcutta-9.

## "SIGCOL"

**LABORATORY GLASSWARE**

*Made of*

BOROSILICATE GLASS HAVING HIGH SILICA AND LOW ALKALI CONTENT WHICH ENSURES RESISTANCE TO THERMAL SHOCK AND CHEMICAL STABILITY

**SARTORIUS**

"SELECTA" BALANCES

Micro and Projection Types

**CARL-ZEISS**

REFRACTOMETERS

SPECTROPHOTOMETERS

STEREO-MICROSCOPES

**MUIRHEAD**

POTENTIOMETER

## "K-9"

**TRIANGULAR BEAM**

CIRCULAR ARRESTMENT

**ANALYTICAL BALANCE**

CAPACITY : 200 Gms.

SENSITIVITY : 1/10 Mgm.

5 Divisions throw of pointer for addition of 1 Mgm.

**CARL-ZEISS**

HAND SPECTROSCOPES

POLARISING MICROSCOPES

METAL MICROSCOPES

POLARIMETERS

MICRO-PHOTO CAMERAS

**LEYBOLD'S**

VACUUM PUMPS

**HEREAUS** - OVENS

**JULIUS PETER** - BOMB CALORIMETER

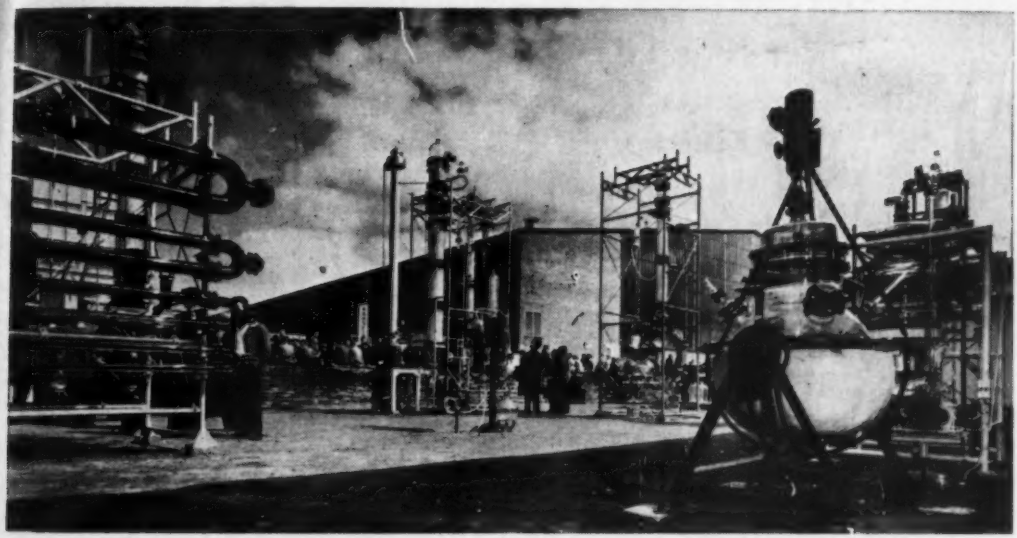
**HOPPLER** - VISCOMETERS

*Distributors :*

**ADAIR, DUTT & Co. (INDIA) PRIVATE Ltd.**

CALCUTTA MADRAS BOMBAY NEW DELHI

J
v
t
S
f
S
l
a
v



# INDUSTRIAL APPARATUS OF JENA GLASS

SCHOTT & GEN MAINZ

JENAER GLAS

## LEADING THE WAY IN SCIENTIFIC GLASS AND APPARATUS MANUFACTURING

JENAER GLASWERK SCHOTT & GEN, the well-known German manufacturing concern with its extensive production of laboratory glasses and apparatus, all-glass constructions for technical plants of chemical and pharmaceutical industries, optical special glasses for different applications as radiation-stabilized optical glasses, interference filters, glasses with hard surface layers resistant to abrasion, radiation shielding glasses for installations of nuclear physics and radio chemistry, glass with a high lead content for Cerenkov counters, water and acid-resistant infrared transmitting arsenic sulphide glass, etc., is providing science and industry with better products which are contributing to greater industrial progress in the world.

Detailed information on apparatus and devices obtainable from :

*Sole Distributors* :

THE SCIENTIFIC INSTRUMENT COMPANY LIMITED

ALLAHABAD • BOMBAY • CALCUTTA • MADRAS • NEW DELHI

# Modified Cellulose Ion-Exchangers

FLOC

POWDER

PAPER

The manufacturers who developed the finest range of papers for laboratory filtration, chromatography and electrophoresis now offer the first comprehensive range of

## Modified Cellulose Ion-Exchangers

CELLULOSE PHOSPHATE · AMINOETHYL-CELLULOSE
CELLULOSE CITRATE · DEAE-CELLULOSE
CARBOXYMETHYL-CELLULOSE · ECTEOLA-CELLULOSE

Specially prepared in three physical forms—floc, powder and paper—they widen the field of application for ion-exchange techniques. These Modified Celluloses differ significantly from ordinary ion-exchange resins. *For further information about their unique properties, please write for the "Ion-Exchange Celluloses General Information" leaflet.*

H. REEVE ANGEL & CO LTD
Gt. Britain: 9 Bridewell Place London EC4
U.S.A: 9 Bridewell Place Clifton N.J.

Sole distributors of

WHATMAN
MATERIALS
Manufacturers W. & R. Balston Ltd

JOURNAL OF THE INDIAN CHEMICAL SOCIETY

JULY, 1960

## Contents

Page

74. The course of cyclisation of α-benzylhomophthalic acids. Part I. A new route to 2 : 3-6 : 7-dibenzotropones.—By J. N. Chatterjea and H. Mukherjee .. 379

75. Chloramine-T as volumetric reagent : Determination of organic derivatives of hydrazone.—By Balwant Singh, S. S. Sahota and R. P. Singh .. 392

76. Cation exchange between colloidal clays and resins in water and aqueous alcohol as a function of the concentration of the dispersed phase.—By Amalesh Chatterjee .. .. .. .. .. .. 395

77. Interaction of charcoal with iodine in aqueous solution.—By Balwant Rai Puri and D. D. Singh .. .. .. .. .. 401

78. Investigations on the reduction of mercuric chloride by oxalic acid induced by potassium persulphate.—By L. K. Saxena and C. P. Singhal .. 405

79. The effect of temperature and viscosity on the fluorescence of solutions of some organic compounds, using UV excitation.—By J. Sahu .. .. 411

80. *p*-Dialkylaminostyryl dyes derived from 5-arylaminothiadiazoles.—By P. B. Tripathy and M. K. Rout .. .. .. .. .. 415

81. Isolation of scopoletin, skimmin and umbelliferone from the trunk-bark of *Skimmia laureola* Hook.—By S. R. Bhattacharjee and D. K. Mullick .. 420

82. Organic pesticides. Part II. Preparation of some *N*-substituted fluorobenzamides.—By K. C. Joshi and S. Giri .. .. .. 423

83. Behaviour of chloronitrobenzenes with hydrazine and hydrazine derivatives. Part X. Preparation of some nitrophenylhydrazines and their hydrazones.—By H. G. Garg and S. S. Joshi .. .. .. 425

84. Synthesis of some substituted sulphathiazoles.—By A. B. Sen and A. K. Roy .. 427

85. Synthesis of α/β-aryl- and γ-aryl-γ-benzyl-γ-butyrolactones.—By D. K. Genge and J. J. Trivedi .. .. .. .. .. 492

86. 4-(Substituted) benzylthiosemicarbazones.—By P. R. Pathan and J. J. Trivedi .. 432

87. Thiazolidones. Part V. Synthesis of 5-alkyl/benzyl-2-arylimino-4-thiazolidones —By B. K. Raval and J. J. Trivedi .. .. .. 435

88. Potential local anaesthetics. Part I. Synthesis of basic *N*-benzylacetamides.—By Miss S. L. Dalal and J. J. Trivedi .. .. .. .. 437

Short Notes :

6. Swietenine, the non-bitter principle of the seeds of *Swietenia macrophylla* King.—By S. Ghosh, T. Chakrabartty and Mrs. A. Chatterjee .. 440

7. Spot test for iron by substituted violuric acids.—By R. P. Singh .. .. 442

# Information for Authors

1. All papers intended for publication in the Journal of the Indian Chemical Society should be addressed to the Hony. Secretary, Indian Chemical Society, 92, Acharya Prafulla Chandra Road, Calcutta-9.

2. *A paper will not normally be considered for publication in the journal unless at least one of the author or authors is (are) either a Fellow or Associate member of the Society.*

3. Communications which have appeared in any other journal shall not be published in this Journal unless this course is specially approved by the Council.

4. Normally an article or original paper should not exceed 15 foolscap pages. *All papers should be submitted in duplicate in typescript* with double line and marginal spacings. Tables and foot notes add considerably to the cost of printing; authors are requested therefore not to use them unless necessary.

5. *All papers should be carefully revised and should be absolutely in final form of printing.* Positions for text-figures should be indicated. Authors are particularly requested to verify references. Authors are solely responsible for the factual accuracy of their papers.

6. Authors should note that the communications are meant for specialists in that field. Extensive review of literature should be avoided. Well-known or previously published procedures followed in the experimental work should only be designated or referred to.

7. Periods of time (unless fractional) and quantities of material should be written in numerals. For economy the abbreviations, cm, c.c., g., m.p., b.p., f.p., calc., exp., Fig., etc., should be used.

8. Authors are requested to enclose line drawings of the diagrams in their papers drawn in India ink on smooth white Bristol board. The drawings should be twice the size they will occupy in the Journal. Authors are particularly requested to reduce the number of diagrams and formulae to an absolute minimum. Organic structural formulae should be arranged to fill the space economically and arrows should be used horizontally or vertically, not diagonally, whenver possible.

9. The reference to literature should be given in brackets in the text and not as a foot-note or at the end and should conform to the normal usages of the *Journal* as regards order and punctuations, and to the abbreviations as given by Chemical Abstracts in its "List of Periodicals Abstracted". Thus, Name or names of authors, Name of Journal (abbreviated, with a single underline; year of publication; number of volume (double underline) and lastly page, e.g., Karrer and Schlieutz, *Helv. Chim. Acta*, 1934, **17**, 7.

The words and lines that will appear in italics in print should be underlined.

10. Authors are expected to be familiar with the normal rules of nomenclature but in case of doubt may refer to "Modern Chemical Nomenclature (Smith, *J. Chem. Soc.* 1936, 1067).

11. New compounds should be indicated by underlining the name at its first mention (excluding Headings) in the experimental section and by giving analytical results in the form: "(Found :———; ———. ——— requires———%)" Analytical results for compounds which have been previously known should be given in the form: "(Found :———; ———. Calc. for ———; ———; ———%)".

12. *Every paper must be accompanied by a short abstract* giving briefly the objects of the investigation, the results obtained and their bearing on chemical knowledge in general. It should be such as to enable any chemist to obtain a clear idea of the investigation and normally should not exceed 250 words.

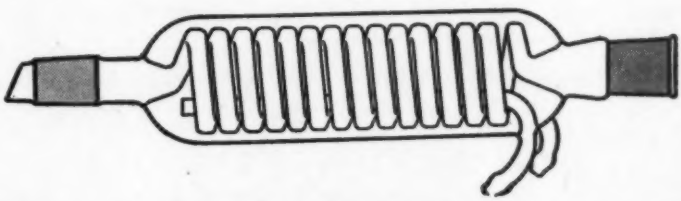
13. The address to which the proofs are to be sent should be written on every paper. One slip-proof or if possible a page-proof will be sent to authors, *which should be returned within a week to the Hony. Secretary, failing which it will be directly printed.*

14. Authors will get 50 copies of reprints free of charge and extra 25 copies on payment of Re. 1/- per page. Extra copies of reprints over 75 copies will be charged at Rs. 5/- per page. Cost of paper and binding, extra. If extra copies are required, the author should intimate the Hony. Secretary, at the time of returning the corrected proofs.

**15. Notes will be given priority in publication.**

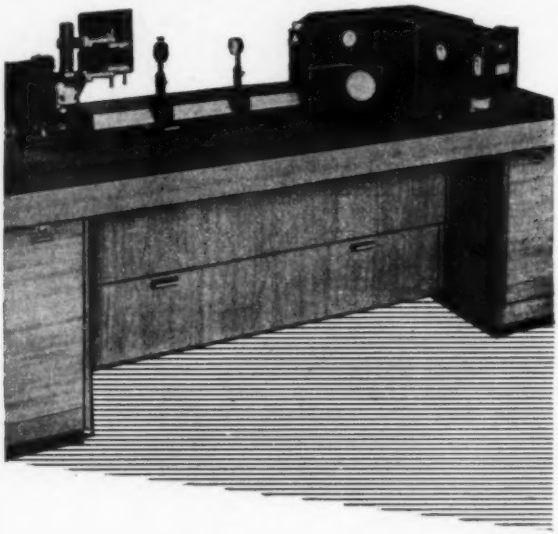
---


# Science Emporium



**Specialist in Manufacturing of all kinds of Scientific Lamp, blown Glass Apparatus from "PYREX" and other "HEAT-RESISTANCE" Glass as per any Specification.**

**39/3, CANAL WEST ROAD, CALCUTTA-4.**



**ZEISS THREE-PRISM GLASS SPECTROGRAPH**

**A Glass Spectrograph with Foersterling set of Prisms of High Power and Resolving Capacity. Large Dispersion and Excellent Definition of Lines. Self contained construction.**

**Equipped with 3 Cameras**

**Camera f=12 cm, F/2.4 and Camera f=27 cm, F/5.4 for Feeble-light Phenomena (Raman effect, Fluorescence or Flame Spectra, etc.)**

**Autocollimation Camera f=130 cm, F/2.6 for Taking Complex Emission Spectra in the Visible Region (Special-type Steels, Rare Earths, etc.)**

**Solves Odd Spectro-Chemical Problems of Organic and Inorganic Nature.**

CARL ZEISS JENA

VEB CARL ZEISS JENA
(German Democratic Republic)

*Sole Agents in India :*

**GORDHANDAS DESAI PRIVATE LTD.**

**PHEROZESHAH MEHTA ROAD, BOMBAY-1.**

*Branches :*

**P-7, Mission Row Extension, CALCUTTA 1.**

**4/2B, Asaf Ali Road, NEW DELHI.**

**22, Linghi Chetty Street, MADRAS 1.**

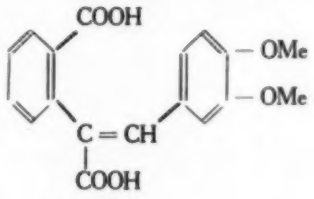
[Jour. Indian Chem. Soc., Vol. 37, No. 7, 1960]

# THE COURSE OF CYCLISATION OF α-BENZYLHOMOPHTHALIC ACIDS. PART I. A NEW ROUTE TO 2:3-6:7-DIBENZOTROPONES

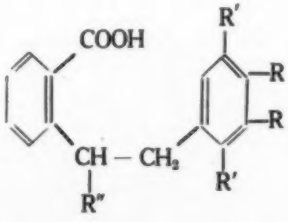
BY J. N. CHATTERJEA AND H. MUKHERJEE

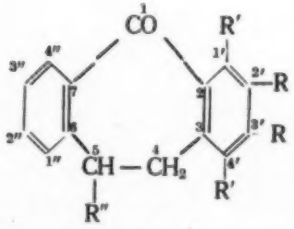
It is shown that cyclisation of α-benzylhomophthalic acids leads either to a seven-membered ketone (source of 2:3-6:7-dibenzotropones) or to an indeno-(3':2'-3:4)isocoumarin or to a mixture of both. Structures of both the classes of compounds have been established. An alternative route to dibenzotropones from α-benzylhomophthalic acids has been indicated.

The synthesis of 2:3-6:7-dibenzotropone and its derivatives was reported by Treibs and Klinkhammer (*Chem. Ber.*, 1951, **84,** 671 ; 1950, **83,** 367) and also independently by Cope and Fenton (*J. Amer. Chem. Soc.*, 1951, **73,** 1673) by essentially the same route. Since then several syntheses have appeared (Bergmann and Ginsburg, *Bull. Res. Council, Israel*, 1951, **1,** No. 3, 120 ; Bergmann *et al.*, *Bull. Soc. Chim.*, 1951, **18,** 684 ; Sorrie and Thomson, *J. Chem. Soc.*, 1955, 2244 ; Battersby and Binks, *ibid.*, 1955, 2896 ; Rigaudy and Nedelec, *Compt. rend.*, 1953, **236,** 1287 ; Leonard *et al.*, *J. Amer Chem. Soc.*, 1955, **77,** 5078 ; Colonge and Sibeud, *Compt. rend.*, 1952, **234,** 530) and an alicyclic approach to 2:3-6:7-dibenzotropone itself has been reported by Amiel and Ginsburg (*Tetrahedron*, 1957, **1,** 19). It appears that an alternative direct synthesis of dibenzotropones may be effected by cyclisation of α-benzylhomophthalic acids which are readily obtained by the reduction of benzylidenehomophthalic acids. The latter are easily prepared



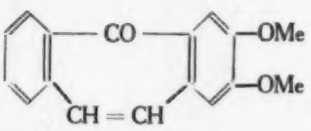

(I)




(II): R=OMe ; R′=H ; R″=COOH.
(III): R=OEt ; R′=H ; R″=COOH.
(IV): R=H ; R′=Me ; R″=COOH.
(V): R=H ; R′=OMe ; R″=COOH.
(VI): R=R′=R″=H.
(VII): R=R″=H ; R′=Me.

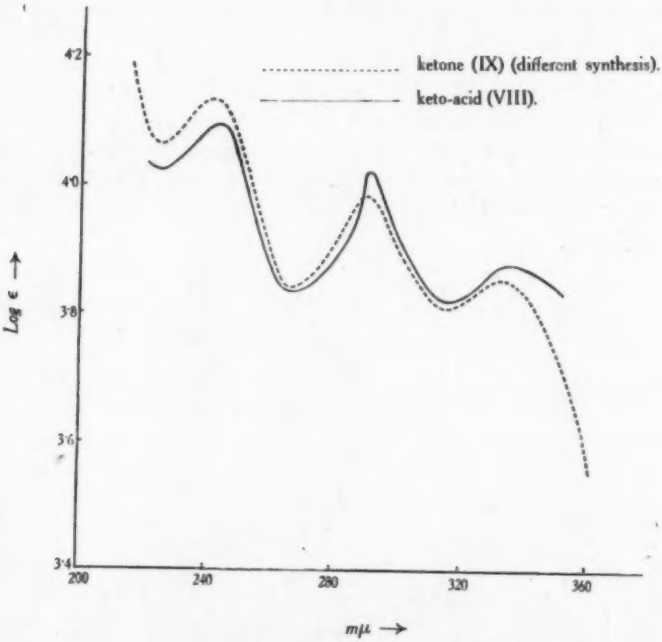
(VIII): R=OMe ; R′=H ; R″=COOH.
(IX): R=OMe ; R′=R″=H.
(X): R=OEt ; R′=H ; R″=COOH.
(XI): R=OEt ; R′=R″=H.
(XII): R=R″=H ; R′=Me.



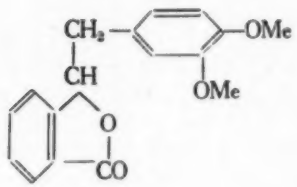

(XIII)

by either Perkin's reaction or by the Stobbe condensation of aromatic aldehydes with homophthalic esters (Pinder and Jones, *J. Chem. Soc.*, 1958, 2612). Thus, veratrylidenehomophthalic acid (I) (Buu Hoï, *Compt. rend.*, 1946, **211,** 643) on reduction with sodium amalgam furnished 3:4-dimethoxybenzylhomophthalic acid (II). This on treatment with polyphosphoric acid at 100° afforded 2′:3′-dimethoxy-2: 3-6: 7-dibenzo-1-suberone-5-carboxylic acid (VIII), the structure of which was followed by comparison of UV spectra (Fig. 1) with the related suberone (IX)

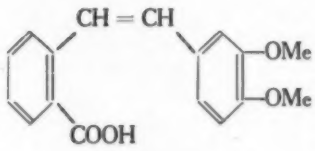
FIG. 1



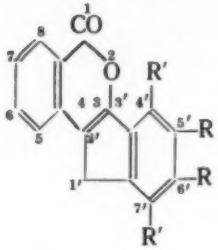

which was synthesised independently as given below. Decarboxylation of (VIII) with the aid of copper bronze also afforded (IX) which on dehydrogenation with *N*-bromosuccinimide yielded the dimethoxydibenzotropone (XIII). The ketone (IX) was secured by using the method of Treibs and Klinkhammer (*loc. cit.*). Thus veratrylidenephthalide (Kodama, *J. Pharm. Soc., Japan*, 1943, **63,** 54) on catalytic reduction or by reduction with zinc dust and potassium hydroxide gave the dihydro derivative (XIV). This on treatment with potassium hydroxide at 200° under carefully controlled conditions furnished the stilbene carboxylic acid (XV) which on catalytic hydrogenation, followed by cyclisation with polyphosphoric acid, readily afforded the ketone (IX).

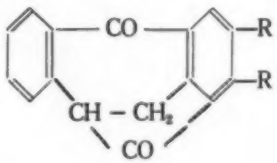


(XIV)



(XV)





(XX)

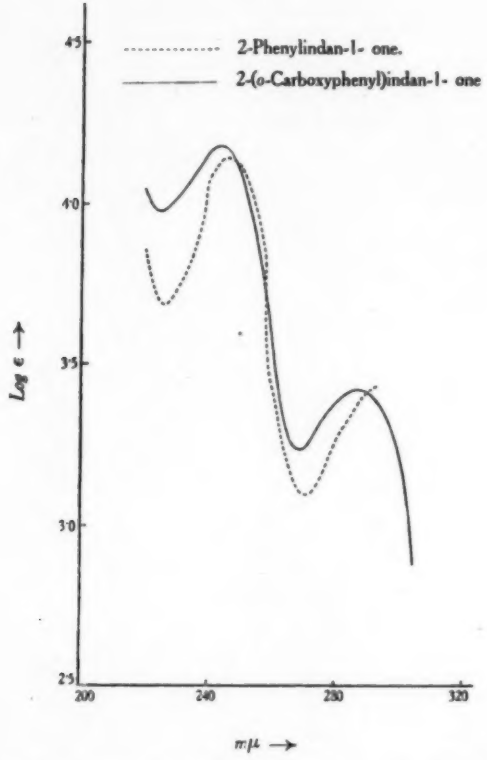
(XVI): R=OEt ; R′=H.
(XVII): R=R′=H.
(XVIII): R=H ; R′=Me.
(XIX): R=H ; R′=OMe.

When 3 :4-diethoxybenzylhomophthalic acid (III) was treated with polyphosphoric acid, a mixture of the acid (X) and an alkali-insoluble compound, $C_{20}H_{18}O_4$, was isolated ; no crystalline product could be obtained from 3 :4-methylenedioxybenzylhomophthalic acid (Buu Hoï, *Compt. rend.*, 1944, **218,** 942). *A priori,* the structure of the alkali-insoluble compound may be the diketone (XX : R=OEt) or 5′ : 6′-diethoxyindeno-(3′:2′-3 : 4) *iso*coumarin (XVI). The formation of diketones by acylation, *meta* to the carbonyl group, is well known in literature (cf. v. Braun and Wissbach, *Ber.*, 1931, **64,** 1785 ; Manske, *J. Amer. Chem. Soc.*, 1931, **53,** 1104). In order to investigate the formation of "diketone" in the simplest case, the cyclisation of benzylhomophthalic acid itself was studied. This compound formed only the anhydride at 100°, but at 150° a single compound, $C_{16}H_{10}O_2$, corresponding to either (XVII : R=H) or (XX : R=H) was readily isolated. The compound dissolved in sulphuric acid producing a brilliant green fluorescent solution and it also reacted with hydroxylamine to give rise to a product, $C_{16}H_{11}NO_2$, corresponding to a monooxime. The compound, however, showed a sharp lactone carbonyl absorption at 5.78μ (KBr pellett) supporting the structure (XVII : R=H). This was further confirmed on the following grounds :

(*i*). 2 : 5-Dimethylbenzylhomophthalic acid (IV) and 2 : 5-dimethoxybenzylhomophthalic acid (V) also underwent double cyclisation with polyphosphoric acid to yield respectively (XVIII) and (XIX), indicating thereby that *one nuclear cyclisation had taken place* and thus excluding the diketone structure.

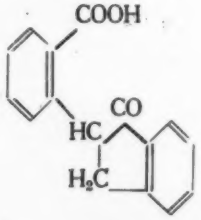
(*ii*). The compound $C_{16}H_{10}O_2$ derived from benzylhomophthalic acid was lactonic in nature and was hydrolysed to the ketone (XXI) (2-*o*-carboxyphenylindan-1-one) having a similar UV spectrum as 2-phenylindan-1-one (Fig. 2).

FIG. 2

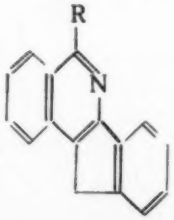



(*iii*). The compound, on treatment with alcoholic ammonia at 200° furnished the hydroxy*iso*quinoline (XXII) which was successively converted into the chloro derivative (XXIII) (by phosphorus oxychloride) and then catalytically reduced to 1 : 2-benzo-4-azafluorene (XXIV).

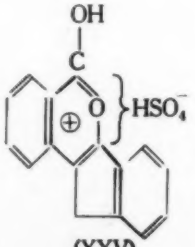
From the above result it appears that the reaction between (XVII) and hydroxylamine resulted in the formation of the *N*-oxide of (XXII). On reduction with zinc dust in acetic acid the compound indeed affords the hydroxy*iso*quinoline (XXII).




(XXI)



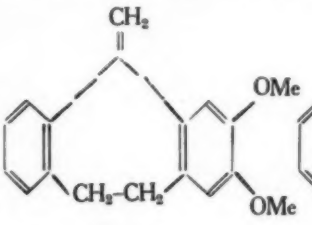

(XXII) : R=OH.
(XXIII) : R=Cl.
(XXIV) : R=H.



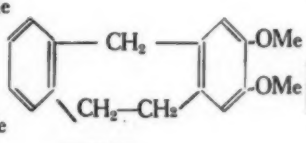

(XXV)

The brilliant green fluorescence of the compound (XVII) in sulphuric acid is due to the formation of 1-hydroxy*iso*benzopyrylium salt (XXV).

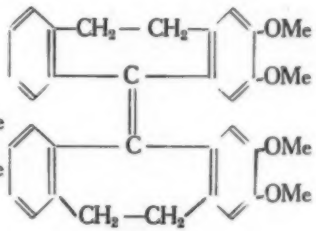
It may be noted that the decarboxylation of α-benzylhomophthalic acid with potassium hydroxide at 300° yields dibenzyl-2-carboxylic acid (in poor yield) (cf. Baker *et al.*, *J. Chem. Soc.*, 1952, 1448). The latter has already been cyclised to dibenzosuberone by Treibs and Klinkhammer. This alternative approach has been used in the synthesis of the suberone (XII), the authentic specimen of which was secured from 2 : 5-dimethylbenzylidenephthalide, following Cope and Fenton (*loc. cit.*). The latter was prepared from 2 : 5-dimethylphenylacetic acid and phthalic anhydride in the usual manner. 2:5-Dimethylphenylacetic acid itself was synthesised from 2 : 5-dimethylbenzaldehyde by way of the related azlactone.



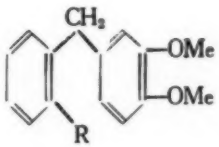
(XXVI)



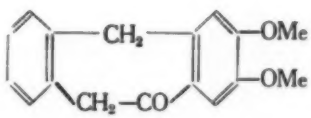
(XXVII)



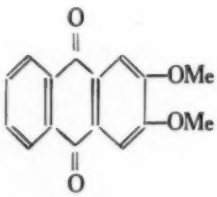
(XXVIII)



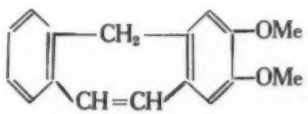
(XXIX) : R = COOH
(XXX) : R = $CH_2OH$
(XXXI) : R = $CH_2CN$
(XXXII) : R = $CH_2COOH$



(XXXIII)



(XXXIV)



(XXXV)

2′ : 3′-Dimethoxy-2:3-6:7-dibenzo-1-suberone (IX) proved similar to 2:3-6:7-dibenzo-1-suberone in chemical properties. Thus, on treatment with methylmagnesium iodide, the compound readily afforded the methylene derivative (XXVI) (absorbing at 11.20 μ in the infrared) and on oxidation with chromic acid gave 2 : 3-dimethoxyanthraquinone (XXXIV), identical with an authentic specimen (vide Experimental). On the Clemmensen reduction, it afforded (XXVI) along with a small quantity of the *bis*-compound (XXVIII) (having stilbene type absorption in UV) which appears to have been formed along with its geometrical isomer. The structure of the former (XXVII) was established by its independent synthesis from *o*-3:4-dimethoxybenzylbenzoic acid (XXIX) (Oliverio, *Gazzetta*, 1934, **64**, 139) which was esterified and reduced with lithium aluminium hydride to the corresponding alcohol (XXX), which was next converted into

the nitrile (XXXI) by way of the related chloromethyl derivative. This indirect method of homologation of (XXIX) had to be resorted to because attempts to prepare the acid chloride of (XXIX) by the action of thionyl chloride in the projected Arndt-Eistert procedure led to the formation of 2 : 3-dimethoxyanthraquinone (XXXIV), evidently formed by a process of oxidation. Hydrolysis of (XXXI), followed by ring-closure, provided 2′: 3′-dimethoxydibenzosuberan-4-one (XXXIII). This ketone was reduced with sodium borohydride to the related carbinol which was dehydrated with the aid of *p*-toluenesulphonic acid to (XXXV) and then catalytically reduced to (XXVII).

The course of cyclisation of several other benzylhomophthalic acids is being communicated in Part II of this series.

## *Experimental

*3:4-Dimethoxybenzylhomophthalic Acid* (II). — Veratrylidenehomophthalic acid (7.5 g.), dissolved in 10% aqueous NaOH solution, was reduced with sodium amalgam (450 g., 4%) and the mixture left at the room temperature with occasional stirring. The alkaline layer on acidification provided a crystalline solid mass which was crystallised from acetic acid in colorless prisms (4.7 g.), m.p. 160-61°. Buu Hoï (*Compt. rend.*, 1944, **218**, 942) records m. p. 153°. (Found : C, 66.0; H, 5.1. $C_{18}H_{18}O_6$ requires C, 65.5; H, 5.5%).

*2′:3′-Dimethoxy-2:3-6:7-dibenzo-1-suberone-5-carboxylic Acid* (VIII).—The above acid (2.59 g.) was treated with polyphosphoric acid (25 g.) at 100° for 1½ hours. The viscous mass was poured into crushed ice when a solid separated on stirring. The *acid* crystallised from ethanol in pale yellow flakes (0.77 g.), m. p. 211° (gas evolution at higher temperature). The compound developed an instantaneous lemon-yellow colour with $H_2SO_4$. (Found: C, 70.0; H, 5.2. $C_{18}H_{16}O_5$ requires C 69.2; H, 5.2%).

*2′:3′-Dimethoxy-2:3-6:7-dibenzo-1-suberone* (IX).—The foregoing acid (0.7 g.) was heated in a metal bath at 240-50° for ½ hour under reduced pressure (100 mm) till the evolution of gas had stopped. The product was cooled, extracted with ether and washed with alkali and water. After drying the ethereal solution ($MgSO_4$), the solvent was removed and the residue was crystallised from ethanol in colorless prismatic needles, m.p. 135°. The ketone showed a lemon-yellow colour with sulphuric acid; yield quantitative. (Found: C, 76.4; H, 6.3. $C_{17}H_{16}O_3$ requires C, 76.1; H, 6.0%).

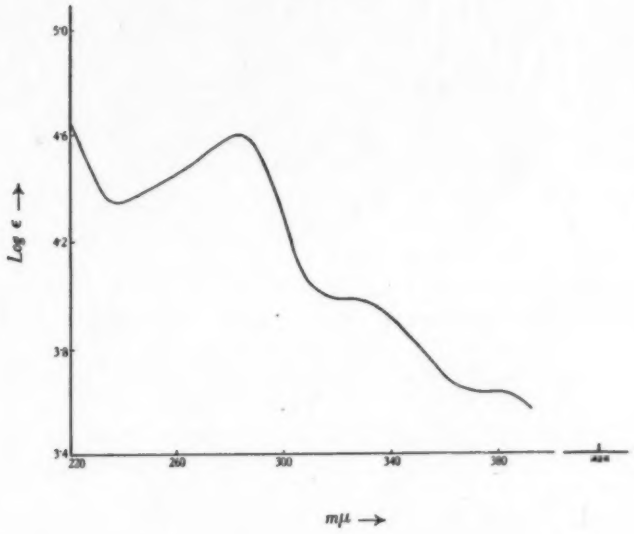
*2′:3′-Dimethoxydibenzotropone* (XIII).—The above ketone (0.5 g.) was dissolved in $CCl_4$ (10 c.c.) and treated with *N*-bromosuccinimide (0.4 g.) and benzoyl peroxide (0.02 g.). The mixture was refluxed for 75 minutes and filtered hot. The filtrate was refluxed with triethylamine (1 c.c.) for 1½ hours. The solution was cooled, treated with water and the *tropone* was crystallised from ethanol in yellow plates, m.p. 131-32°, depressed on admixture with the suberone (IX). The compound dissolved in sulphuric acid exhibiting a lemon-yellow colour. $\lambda_{max}^{alc.}$ 283 mμ (log ε 4.59) (Fig. 3). (Found : C, 76.3; H, 4.9. $C_{17}H_{14}O_3$ requires C, 76.7; H, 5.3 %).

*3:4-Dimethoxybenzylphthalide* (XIV).—(*a*). Zinc dust (7.5 g.) was added in small quantities at a time to a boiling mixture of veratrylidenephthalide (5 g.), water (25 c.c.) and KOH (12.5 g.). The boiling was continued till the solution became colorless (40-50 minutes). Water was added to dissolve the potassium salt and the resulting solution filtered and acidified. The *phthalide*

* All m.p.s are uncorrected. UV absorption spectrum was measured in a Beckman quartz spectrophotometer (DU model).

crystallised from methanol in colorless plates (4.1 g.), m.p. 88-90°. (Found: C, 72.1; H, 5.8. $C_{17}H_{16}O_4$ requires C, 71.8; H, 5.7%).

FIG. 3




(*b*). The veratrylidene phthalide (1.0 g.) was dissolved in ethanol (50 c.c.) and shaken in an atmosphere of hydrogen in presence of palladised charcoal (0.2 g., 5%). The hydrogenation was complete in 1½ hours and on working up, the above dihydrophthalide, m.p. and mixed m.p. 89-91°, was obtained.

*4′:5′-Dimethoxystilbene-2-carboxylic Acid* (XV).—The above reduced phthalide (1 g.) was treated with a solution of KOH (0.5 g.) in water (1 c.c.) and the mixture heated under reduced pressure at 200° (oil-bath) for 1½ hours. The product was dissolved in water and acidified. The *acid* (0.5 g.) separated from 90% acetic acid in colorless plates, m.p. 186°. (Found: C, 72.1; H, 5.7. $C_{17}H_{16}O_4$ requires C, 71.8; H, 5.7%).

*4′:5′-Dimethoxydibenzyl-2-carboxylic Acid.*—The foregoing acid (XV, 4.51 g.) was reduced catalytically in presence of palladised charcoal (0.5 g., 15%) in acetic acid (15 c.c.). After the reduction was complete (½ hour) the mixture was worked up, yielding the *acid* (3.6 g.) in colorless prisms, m.p. 140-41°. (Found: C, 71.5; H, 6.5. $C_{17}H_{18}O_4$ requires C, 71.3; H, 6.3%).

*2′:3′-Dimethoxy-2:3-6:7-dibenzo-1-suberone* (IX.)—The above acid (4. g.) was added to polyphosphoric acid (35 g.) and heated at 100° for 1 hour and then poured into crushed ice. The organic matter was taken up in ether, washed with alkali and water, and dried. The solid separating on removal of the solvent was crystallised from ethanol in colorless needles (3.15 g.), m.p. 135-36°, undepressed on admixture with the specimen obtained before. The compound did not furnish any oxime or 2:4-dinitrophenylhydrazone.

*3:4-Diethoxybenzylhomophthalic Acid.*—3:4-Diethoxybenzaldehyde (King *et al.*, *J. Chem. Soc.*, 1952, 21) (6.1g.) and dimethylhomophthalic ester (7.4 g.) were added to a solution of sodium (0.53 g.) in dry methanol (30 c.c.) and refluxed gently for 6 hours. The mixture was cooled and excess of

methanol removed by distillation. Water (36 c.c.) was added to the residue and the mixture extracted with ether to remove the unchanged material. The aqueous layer was heated with a 10% NaOH solution (100c.c.) and then acidified to afford the *homophthalic acid* as a crystalline mass which crystallised from acetic acid in yellowish plates, m.p. 178-79°, yield 6.0 g. (Found: C, 67.7; H, 5.8. $C_{20}H_{20}O_6$ requires C, 67.4; H, 5.7%). On heating with acetic anhydride the acid gave the *anhydride* which crystallised from acetic acid in orange needles, m.p. 146-48°.

The above acid (9.7 g.) was dissolved in a 10% NaOH solution and reduced with sodium amalgam (200 g., 2%) at the room temperature for 48 hours. On working up in the usual manner, 3:4-*diethoxybenzylhomophthalic acid* (III) was obtained in colorless plates (7 g.), m.p. 169-70°. (Found: C, 66.8; H, 6.2. $C_{20}H_{22}O_6$ requires C, 67.0; H, 6.2%).

*Cyclisation of* (III).—The foregoing acid (III, 5.5 g.) was treated with polyphosphoric acid (40 g.) and heated at 100° for 2 hours. The resulting dark red solution was poured into crushed ice and vigorously stirred when a greenish solid separated. This was filtered, triturated with $NaHCO_3$ solution and filtered. The insoluble residue was dissolved in ether, washed with $NaHCO_3$ solution and water, dried and the ether removed. 5′:6′-*diethoxyindeno*-(3′:2′-3:4)*isocoumarin* (0.9 g.) was obtained on removal of the ethereal solution. It was crystallised from acetic acid in yellow, woolly needles, m.p. 176-77°. The compound produced a brilliant green fluorescent solution in sulphuric acid. (Found: C, 75.0; H, 5.8. $C_{20}H_{18}O_4$ requires C, 74.5; H, 5.6%).

The yellow alkaline solution (filtrate) was acidified and the solid obtained was crystallised from acetic acid. 2′:3′-*Diethoxy*-2:3-6:7-*dibenzo*-1-*suberone*-5-*carboxylic acid* (0.7 g.) crystallised from acetic acid in yellowish plates, m.p. 165° (gas evolution at higher temperature). (Found: C, 69.9; H, 5.5. $C_{20}H_{20}O_5$ requires C, 70.6; H, 5.9%). Decarboxylation of this acid (0.45 g.) was done by heating in a metal bath at 250° for ½ hour under reduced pressure (3 mm). The product was cooled, extracted with ether, washed with sodium carbonate solution and water, dried and the solvent removed. 2′:3′-*Diethoxy*-2:3-6:7-*dibenzo*-1-*suberone* (XI) crystallised from ethanol in yellow needles, m.p. 91-92°, yield 0.12 g. (Found: C, 76.4; H, 6.9. $C_{19}H_{20}O_3$ requires C, 77.0; H, 6.8%).

2:3-*Diethoxydibenzotropone*.—The above ketone (XI, 0.11 g.) was dehydrogenated by *N*-bromosuccinimide (0.08 g.) as before. The product after treatment with triethylamine was obtained as a semisolid mass. For purification, it was chromatographed on alumina column in benzene solution when most of the impurities were held back. The *tropone* was crystallised from ethanol in yellowish needles, m.p. 86°, depressed to 75° on admixture with the foregoing ketone (XI). (Found: C, 77.7; H, 6.3. $C_{19}H_{18}O_3$ requires C, 77.5; H, 6.2%).

α-*Benzylhomophthalic Anhydride*.—Benzylhomophthalic acid (0.2 g.) was heated at 180° in an oil-bath. After the evolution of water vapour was complete, the mass was cooled and the anhydride crystallised from benzene in colorless prisms, m.p. 115°. (Found: C, 75.8; H, 5.0. Calc. for $C_{16}H_{12}O_3$: C, 76.2; H, 4.8%). The compound formed a yellow solution with NaOH (formation of enolic salt).

*Cyclisation of* α-*Benzylhomophthalic Acid*.—Benzylhomophthalic acid (1.0 g.) was heated with polyphosphoric acid (10 g.) at 150-60° for 12 hours. The resulting mass was poured into crushed ice and the solid separating was collected and crystallised from acetic acid. *Indeno*-(3′: 2′-3: 4)-*isocoumarin* (XVII) was obtained in cream-coloured plates, m.p. 169-71°, showing a green fluorescence in $H_2SO_4$ (conc.), yield 0.6 g. $\lambda_{max}^{alc}$ 224 mμ (log ε 4.24), 234 (log ε 4.28), 310 (log ε 4.31), 342 (log 3.96) and 350 mμ (log ε 3.95). (Found: C, 82.1 ; H, 4.4. $C_{16}H_{10}O_2$ requires C, 82.0; H, 4.3 %). The compound did not furnish any 2: 4-dinitrophenylhydrazone or phenylhydrazone. On treatment with hydroxylamine hydrochloride in pyridine solution for 4.5 hours on the

water-bath, the *N*-oxide of (XXII), crystallising from acetic acid in brownish needles, m.p. 260° (decomp.), was isolated. $\lambda_{max}^{alc}$ 238 (log ε 4.38), 253 (log ε 4.21), 262 (log ε 4.18), 284 (log ε 3.79), 288 (log ε 3.78) and 338 mμ (log ε 4.21). (Found: C, 76.4; H, 4.1; N, 5.7. $C_{16}H_{11}O_2N$ requires C, 77.1; H, 4.4; N, 5.6%). On reduction with zinc dust in acetic acid for 4 hours, the hydroxy*iso*quinoline (XXII) was isolated.

2:5-*Dimethylbenzylhomophthalic Acid* (IV).—A mixture of 2:5-dimethylbenzaldehyde (Hinkel *et al.*, *J. Chem. Soc.*, 1932, 2793) (3.15 g.) and diethyl homophthalate (5.8 g.) was added to methanolic sodium methoxide solution (0.5 g. of sodium in 15 c.c. of methanol) and refluxed gently for 6 hours. On working up in the usual manner, the *benzylidene derivative* (7.0 g.) was isolated, crystallising from acetic acid in colorless needles, m.p. 213-14°. (Found: C, 72.6; H, 5.2. $C_{18}H_{16}O_4$ requires C, 73.0; H, 5.4%). Reduction of this acid (5.0 g.) with sodium amalgam (150 g., 3%) at the room temperature for 48 hours provided the reduced *acid* (IV) which was crystallised from acetic acid in colorless plates, m.p. 177-78° (evolution of gas), yield 4.1 g. (Found: C, 72.5; H, 6.3. $C_{18}H_{18}O_4$ requires C, 72.5; H, 6.1%).

4′:7′-*Dimethylindeno-* (3′:2′-3:4)-iso*coumarin* (XVIII).—The foregoing acid (1.0 g.) was heated with polyphosphoric acid (25 g.) at 100° for 5 hours and then worked up in the usual manner. The iso*coumarin* crystallised from acetic acid in a yellowish crystalline mass, m.p. 188-90°. The compound is insoluble in cold alkali and showed a green fluorescence in $H_2SO_4$ (conc.). $\lambda_{max}^{alc}$ 236 (log ε 4.25), 313 (log ε 4.29), 326 (log ε 4.27) and 362 mμ (log ε 3.96). (Found: C, 82.6; H, 5.5. $C_{18}H_{14}O_4$ requires C, 82.4; H, 5.4%).

2:5-*Dimethoxybenzylhomophthalic Acid* (V).—A mixture of diethyl homophthalate (2.8 g.) and 2:5-dimethoxybenzaldehyde (Tiemann and Müller, *Ber.*, 1881, **14**, 1992) (2 g.) was added to a solution of sodium (0.2 g.) in dry methanol (17 c.c.), and the solution refluxed for 6 hours. Isolated as usual, the 2:5-*dimethoxybenzylidenehomophthalic acid* (4.8 g.) crystallised from acetic acid in glistening yellow plates, m.p. 214-15° (gas evolution). (Found: C, 65.7; H, 5.1. $C_{18}H_{16}O_6$ requires C, 65.9; H, 4.9%). This acid (3.75 g.) on reduction with sodium amalgam (280g., 2%) as before, gave the *benzylhomophthalic acid* (V) in quantitative yield. This crystallised from acetic acid in a colorless mass, m.p. 168-69°. (Found: C, 65.1; H, 5.7. $C_{18}H_{18}O_6$ requires C, 65.5; H, 5.5%).

*Cyclisation of* (V).—The reduced acid (0.5 g.) was heated with polyphosphoric acid (20 g.) at 80° for 17 hours. The sticky mass separating on pouring into ice was crystallised from acetic acid in yellow needles (0.05 g.). On recrystallisation, 4′: 7′-*dimethoxyindeno*-(3′:2′-3:4)-iso*coumarin* (XIX) was isolated, m.p. 238-39°. The compound is insoluble in cold dilute alkali. (Found: C, 73.6; H, 5.0; OMe, 22.5. $C_{18}H_{14}O_4$ requires C, 73.5; H. 4.8; 2OMe, 21.1%).

2-*o*-*Carboxyphenylindan*-1-*one*.—The indeno*iso*coumarin (XVII) (0.5g.) was hydrolysed with EtOH-KOH on a water-bath for 1 hour and after removal of the alcohol it was carefully acidified. The *ketone* (XXI) crystallised from ethanol in colorless prisms, m.p. 160° (gas evolution). It gave the same green fluorescent solution in sulphuric acid as the indeno*iso*coumarin, obviously due to lactonisation. $\lambda_{max}^{alc}$ 244 (log ε 4.18) and 288 mμ (log ε 3.42). (Found: C, 76.3; H, 5.0. $C_{16}H_{12}O_3$ requires C, 76.2; H, 4.8 %). The *oxime*, prepared in pyridine, darkens and melts at 238° (decomp.). (Found: N, 5.6. $C_{16}H_{13}O_3N$ requires N, 5.2%).

2-*Phenylindan*-1-*one* was synthesised from 1-phenylhydrocinnamic acid by cyclisation with polyphosphoric acid (cf. Miller and Rhode, *Ber.*, 1892, **25**, 2096). $\lambda_{max}^{alc}$ 246 (log ε 4.14) and 294 mμ (log ε 3.42). The 2:4-*dinitrophenylhydrazone* was crystallised from acetic acid in orange needles, m.p. 217-18°. (Found: N, 14.1. $C_{21}H_{16}O_4N_4$ requires N, 14.4%).

*Indeno-(3′: 2′-3: 4)-1-chloroisoquinoline* (XXIII).—The *iso*coumarin (XVII) was heated with ethanolic ammonia (12 c.c., saturated at 0°) at 200° for 5 hours in a sealed tube. The cream-coloured mass of *indeno-(3′: 2′-3: 4)-1-hydroxyisoquinoline* that separated was crystallised from acetic acid and obtained in drab needles, m.p. > 300°; yield quantitative. $\lambda_{max}^{alc}$ 236 (log ε 4.24) and 329 mμ (log ε 4.14). (Found: C, 82.4; H, 4.9. $C_{16}H_{11}ON$ requires C, 82.4 ; H, 4.8%). This hydroxy compound (0.5 g.) was refluxed with $POCl_3$ (12 c.c.) for 1½ hours. The yellowish solution was poured into cracked ice, the entire mass made alkaline with ammonia and then extracted with benzene. The dried benzene solution was filtered through an alumina column, concentrated and the crystalline mass recrystallised from benzene-petroleum ether. The *chloro* compound was obtained in nearly colorless prisms, m.p. 144-45°, yield 0.31 g. The compound does not give a picrate. $\lambda_{max}^{alc}$ 258 (log ε 4.55), 303 (log ε 4.23), 317 (log ε 4.31), 348 (log ε 3.76) and 352 mμ (log ε 3.78). (Found: C, 76.2; H, 4.1. $C_{16}H_{10}NCl$ requires C, 76.4; H, 4.0%).

1 : 2-*Benzo-4-azafluorene* (XXIV).—The above chloro derivative (0.2 g.) was reduced with palladised charcoal (0.2 g., 5%) in methanol in presence of KOH (0.1 g.) in an atmosphere of hydrogen at the room temperature. Absorption of hydrogen (18 c.c.) was complete in 15 minutes. The mixture was filtered, concentrated, cooled, and the *azafluorene* precipitated by water. The compound was crystallised from methanol in colorless prisms, m. p. 163-64°, yield quantitative. $\lambda_{max}^{alc}$ 258 (log ε 4.59), 299 (log ε 4.25), 312 (log ε 4.31) and 344 mμ (log ε 3.72). (Found : C, 87.9 ; H, 5.1. $C_{16}H_{11}N$ requires C, 88.4 ; H, 5.1 %). The *picrate* crystallised from a large volume of ethanol in yellow prisms, m. p. 234-35° (decomp.). (Found : N, 9.3. $C_{16}H_{11}N$. $C_6H_3O_7N_3$ requires N, 9.7 %). The *picrolonate* was crystallised from acetic acid in yellow mass, m.p. 252° (decomp.).

*Decarboxylation of α-Benzylhomophthalic Acid.*—The acid (0.5 g.) was added to fused KOH (3.7 g.) and the temperature maintained for 5 minutes at 350° (metal bath). The mixture was cooled, dissolved in water and the alkaline solution filtered. On acidification, the filtrate gave a colorless mass of dibenzyl-*o*-carboxylic acid which crystallised from ethanol in colorless prisms, m. p. 127-29°(lit., m. p. 129-30°).

Similar decarboxylation of 2 : 5-dimethylbenzylhomophthalic acid afforded 2′ : 5′-dimethyl-dibenzyl-2-carboxylic acid in rather a very poor yield, m. p. 116° (*vide infra*).

2:5-*Dimethylphenylacetic Acid.*—2:5-Dimethylbenzaldehyde (32 g.) was condensed with hippuric acid according to the procedure given for the synthesis of homoveratric acid ("Organic Synthesis", Coll. Vol. II, p. 333). The *azlactone* (30 g.) was crystallised from acetic acid in cream-coloured plates, m. p. 124-25°. (Found : N, 5.2. $C_{18}H_{15}O_2N$ requires N, 5.1%). Hydrolysis of the azlactone and the oxidation of the resulting pyruvic acid gave a mixture of benzoic acid and 2 : 5-dimethylphenylacetic acid which were separated by fractional distillation of the methyl esters (b. p. of the latter, 170-72°/ 80 mm). Hydrolysis with alkali, followed by acidification, furnished 2 : 5-*dimethylphenylacetic acid* which crystallised from acetic acid in colorless plates, m. p. 130°. (Found : C, 73.2 ; H, 7.3. $C_{10}H_{12}O_2$ requires C, 73.1 ; H, 7.4 %). The *anilide* of this acid crystallised from ethanol in colorless needles, m. p. 146. (Found : N, 6.3. $C_{16}H_{17}ON$ requires N, 5.9 %).

2 : 5-*Dimethylbenzylidenephthalide.*—A mixture of the above acid (1.2 g.), phthalic anhydride (1.0 g.) and fused sodium acetate (0.03 g.) was heated in a diethyleneglycol bath for 3 hours. The entire mass was poured into ethanol and the yellowish needles of the *phthalide* (0.7 g.) was crystallised from acetic acid in lemon-yellow prisms, m.p. 153-54°. (Found : C, 81.0 ; H, 5.7. $C_{17}H_{14}O_2$ requires C, 81.6 ; H, 5.6%).

2 : 5-*Dimethyldibenzyl-2-carboxylic Acid* (VII).—A solution of the foregoing phthalide (1.0 g.) in acetic acid (5 c.c.) was refluxed with hydriodic acid (12 c.c.) and phosphorus (0.5 g.) for 6 hours. A heavy liquid separated during this period. The mixture was poured into water when a solid mass separated. This was extracted with ammonia and the ammoniacal solution on acidification furnished the *acid* (VII) (0.4 g.), crystallising from acetic acid in colorless prisms, m. p. 117°. (Found : C, 80.0 ; H, 7.3. $C_{17}H_{18}O_2$ requires C, 80.3 ; H, 7.1%). The ammonia-insoluble residue contained the related *dihydrophthalide* which was extracted with ethanol and crystallised from ethanol in colorless glistening plates, m. p. 109-10°, yield 0.4 g. (Found : C, 80.5 ; H, 6.3. $C_{17}H_{16}O_2$ requires C, 80.9 ; H, 6.3 %).

1′:4′-*Dimethyl-2:3-6:7-dibenzo-1-suberone* (XII).—Poor result was obtained when the above acid was cyclised with polyphosphoric acid. The foregoing acid (0.9 g.) was converted into the acid chloride by thionyl chloride (1 c.c.) in the usual manner. After removing thionyl chloride in vacuum, the residue was dissolved in dry carbon disulphide (10 c.c.) and treated with aluminium chloride (1.5 g.) and left at the room temperature. On working up the product after 12 hours, the *suberone* was obtained in the neutral fraction (b. p. 183°/1.5 mm) solidifying on cooling. This crystallised from ethanol in colorless prisms, m. p. 80-81°, developing a lemon-yellow coloration with sulphuric acid ; yield 0.5 g. (Found : C, 86.3 ; H, 6.9. $C_{17}H_{16}O$ requires C, 86.4 ; H, 6.8%).

2′:3′-*Dimethoxy-2:3-6:7-dibenzo-1-methylenesuberan* (XXVI).—A solution of the ketone (IX, 0.1 g,) in ether (15 c.c.) was added dropwise to an excess of methylmagnesium iodide (*ca.* 2 moles). A yellow complex separated at once. After 15 minutes, the mixture was decomposed with $H_2SO_4$ (dil.) and the ethereal solution separated and dried. After removal of the ether, the residual oil was dissolved in benzene (6 c.c.), a trace of *p*-toluenesulphonic acid added and water removed from the boiling solution by distillation. The solid residue, after removal of the benzene, crystallised from methanol, yielding the *suberan* in colorless prisms, m. p. 91°. The compound did not contain any active hydrogen. (Found : C, 81.3 ; H, 7.2. $C_{18}H_{18}O_2$ requires C, 81.2 ; H, 6.8 %).

2:3-*Dimethoxyanthraquinone* (XXXIV).—A solution of the suberone (IX, 0.2 g.) in purified acetic acid (5 c.c.) was treated with a solution of chromic acid (0.4 g.) in acetic acid (5 c.c.). The mixture was warmed on the water-bath for 45 minutes when evolution of gas took place. The whole mass was diluted with water and the material that separated was collected. On washing with dilute alkali, most of the acidic material was removed, leaving an orange residue which on sublimation furnished *dimethoxyanthraquinone* (0.06 g.). The quinone was crystallised from acetic acid in lemon-yellow needles, m. p. 239-40°, undepressed on admixture with an authentic specimen as described below. (Found : C, 71.2 ; H, 4.7. $C_{16}H_{12}O_4$ requires C, 71.6 ; H, 4.5%). The alkaline filtrate on acidification gave a slimy mass which had no tendency to crystallise.

To synthesise the anthraquinone, *o*-veratroylbenzoic acid (1.0 g.) was dissolved in $H_2SO_4$ (15 c.c.) and heated on the steam-bath for ½ hour. On pouring into water the anthraquinone was obtained in quantitative yield, crystallising from acetic acid in yellow needles, m. p. 239-40°.

2:3-*Dimethoxyanthrone* was similarly prepared by the cyclisation *o*-veratrylbenzoic acid. The compound crystallised from acetic acid in light yellow needles, m. p. 130°. (Found : C, 75.2 ; H, 5.4. $C_{16}H_{14}O_3$ requires C, 75.6 ; H, 5.5%).

*2′ : 3′-Dimethoxy-2 : 3-6 : 7-dibenzosuberan* (XXVII).—A mixture of the ketone (IX, 0.5 g.), amalgamated zinc (10 g.), HCl (conc., 10 c.c.) and toluene (15 c.c.) were refluxed for 24 hours. The whole mass was diluted with water, extracted with ether and then the solvents removed under reduced pressure. The oily gummy residue was treated with dry ether (5 c.c.) when the *bis-compound* (XXVIII) (0.05 g.) separated. This crystallised from acetic acid in fluffy mass, m. p. 245-55° with prolonged sintering, indicating that the product was a mixture of the two possible *bis*-compounds. (Found : C, 80.4; H, 6.1. $C_{34}H_{32}O_4$ requires C, 80.9; H, 6.4%). $\lambda_{alc.}^{max.}$ 288 mμ (log ε 4.2). The ethereal filtrate on evaporation gave the *suberan* as a gum which solidified (0.2 g.), crystallising from acetic acid in colorless prisms, m. p. 86-88°. (Found : C, 80.4 ; H, 7.1. $C_{17}H_{18}O_2$ requires C, 80.3 ; H, 7.1%).

*o-Veratrylbenzyl Alcohol* (XXX).—On treating *o*-veratrylbenzoic acid with thionyl chloride, a yellow solution was first obtained which rapidly turned brown and then an orange-coloured compound separated in course of 1½ hours. The product was collected and identified as the anthraquinone (XXXIV), m. p. 239° by direct comparision.

*o*-Veratrylbenzoic acid (10 g.) was esterified with diazomethane. The methyl ester, which did not solidify, was directly reduced by dissolving in dry ether (50 c.c.) and adding it to a slurry of lithium aluminium hydride (3 g.) in ether (50 c.c.). In the beginning there was no appreciable reaction, but the reaction became vigorous towards the end. The mixture was left overnight and next day on working up in the usual manner, *o*-veratrylbenzyl alcohol (8.1 g.) was isolated, crystallising from benzene in prisms, m. p. 82°. (Found: C, 84.6; H, 7.2. $C_{16}H_{18}O_3$ requires C, 74.4; H, 7.0%).

*o-Veratrylbenzyl Cyanide* (XXXI).—A solution of the foregoing alcohol (4.0 g.) in benzene (5 c.c.) was treated with phosphorus pentachloride (3.0 g.). A vigorous reaction took place at the ordinary temperature. After ½ hour, the mixture was decomposed with ice, extracted with ether and washed with water. After removal of the ether, the residue was treated with a solution of potassium cyanide (2.0 g.) in water (5 c.c.) and ethanol (2 c.c.). The mixture was refluxed for 3 hours, and on working up in the usual manner a semisolid mass of the *cyanide* was obtained which was filtered, washed with cold ethanol and crystallised from methanol. The compound was obtained in hard prisms, m. p. 102-103°, yield 2.1 g. (Found : N, 5.6. $C_{17}H_{17}O_2N$ requires N, 5.2%).

*2′:3′-Dimethoxydibenzosuberan-4-one* (XXXIII).—A mixture of the above cyanide (3 g.), acetic acid (5 c.c.), water (5 c.c.) and sulphuric acid (5 c.c.) was boiled under reflux for 4 hours. The mixture was poured into water, extracted with ether and the acidic material extracted with sodium hydrogen carbonate. This carbonate solution on acidification gave the phenylacetic acid (XXXII) as a gum (2 g.) which had no tendency to crystallise. This was next heated with polyphosphoric acid (10 g.) at 110° for 1½ hours. On working up, the neutral matter solidified affording the *suberone* (XXXIII) which crystallised from methanol in colorless leaflets, m. p. 168°, yield 0.6 g. (Found : C, 76.5 ; H, 6.3. $C_{17}H_{16}O_3$ requires C, 76.1 ; H, 6.0%). The *oxime*, prepared in pyridine, was crystallised from methanol in colorless leaflets, m. p. 190°. (Found : C, 72.5 ; H, 6.1. $C_{17}H_{17}O_3N$ requires C, 72.1 ; H, 6.1%).

*2′ : 3′-Dimethoxy-2 : 3-6 : 7-dibenzosuberan* (XXVII).—The above ketone (0.16 g.) in methanol (5 c.c.) was treated with sodium borohydride (0.2 g.), added in small portions, and then left overnight. After removing methanol, the residue was treated with aqueous acetic acid when crystals of the *carbinol* (m. p. of the crude material, 225-26°) separated. This was collected,

dried, dissolved in toluene (6 c.c.) and boiled with the addition of *p*-toluenesulphonic acid (3 mg.). Water was removed from the system by careful distillation (3 hours). On cooling, 2′: 3′-*dimethoxydibenzosuberene*-4 (XXXV) separated (0.12 g.) which crystallised from acetic acid in silky needles, m. p. 251-53°. (Found : C, 81.3 ; H, 6.7. $C_{17}H_{16}O_2$ requires C, 80.9 ; H, 6.4%).

A solution of the suberene (0.1 g.) in acetic acid (5 c.c.) was hydrogenated at the room temperature and atmospheric pressure in the presence of palladised charcoal (0.05 g., 5%). The absorption of hydrogen was rapid and complete in 2 minutes. On working up, the compound (XXVII) was obtained as colorless prisms, m. p. 91°, from acetic acid, identical with the suberan prepared previously.

The authors wish to thank the authorities of the Patna University for a generous grant.

Chemical Laboratory,
Science College, Patna-5.

*Received February* 18, 1960.

[Jour. Indian Chem. Soc., Vol. 37, No. 7, 1960]

# CHLORAMINE-T AS VOLUMETRIC REAGENT: DETERMINATION OF ORGANIC DERIVATIVES OF HYDRAZINE

By Balwant Singh, S. S. Sahota and R. P. Singh

In presence of hydrochloric acid chloramine-T solution has been used as a volumetric reagent for the determination of semicarbazide hydrochloride, benzal semicarbazone, *o*-nitro-, *m*-nitro-, *o*-hydroxy-, *p*-methoxy-, *p*-chloro-, and *o*-chlorobenzal semicarbazones, acetone semicarbazone, benzoylhydrazine, benzalazine, 4-phenylsemicarbazide hydrochloride, thiosemicarbazide, phenylhydrazine hydrochloride and β-formylphenylhydrazine.

In visual titrations iodine monochloride-chloroform was used as an indicator. In potentiometric titrations, platinum electrode was used as an oxidation-reduction electrode and it was coupled with a saturated calomel electrode. At equivalence point there is a sharp jump in potential in each titration.

Noll (*Chem. Ztg.*, 1924, **48,** 485) described the use of chloramine-T [$p$-$CH_3C_6H_4SO_2N$-(Na) $Cl.3H_2O$, M. W. 281.5] as an oxidising agent. In solution it behaves as a stable hypochlorite. The reagent is finding an increasing use in place of sodium hypochlorite. It has the advantage that its aqueous solution is stable in air and shows little deterioration over long periods, when kept in stoppered dark bottles; moreover, as alkali is absent there is no risk of the formation of chlorates which lead to side reactions.

Rupp (*Pharm. Zentrl.*, 1925, **66,** 33) used chloramine-T for the determination of antimony and stannous tin. Tomicek and Sucharda (*Chem. Abst.*, 1932, **26,** 1210) used it as a reagent for the potentiometric determination of arsenic, antimony, stannous tin, ferrous iron, ferrocyanide and iodide, and for visual titrations of antimony and arsenic using methyl red as indicator. Komarovskii *et al.* (*J. Appl. Chem.*, USSR, 1933, **6,** 742; *Z. anal. Chem.*, 1946, **96,** 321) have shown that chloramine-T can be used as a volumetric reagent to replace the more expensive iodine and less stable hypochlorite in the estimation of ferrocyanide, hydrazine and hypophosphite. Singh and Rehman (this *Journal*, 1940, **17,** 170) used this reagent for the potentiometric determination of sodium nitrite, sodium bisulphite, hydrazine hydrochloride and potassium iodide.

Lee *et al.* (*Anal. Chem.*, 1948, **20,** 431) used chloramine-T in the quantitative estimation of various organic sulphides. Afanas'ev (*J. Phys. Chem.*, USSR, 1948, **22,** 499) studied the oxidation-reduction potential and the mechanism of oxidation with chloramine-T and used it for the volumetric estimation of various organic compounds using indigo carmine and methyl red as indicators.

Singh *et al.* (*Res. Bull. East Panjab Univ.*, 1953, **30,** 55) have used chloramine-T for the potentiometric estimation of vanillin, *p*-hydroxybenzaldehyde, benzaldehyde, salicylaldehyde, acetaldehyde, furfural, urea, oxalic acid, thiourea, glycerol and mannitol. Singh and Sood (*Anal. Chim. Acta*, 1955, **13,** 30) have further extended the use of chloramine-T for the estimation of potassium iodide, hydrazine sulphate, mercurous chloride, arsenious oxide, stannous chloride, tartar emetic, potassium thiocyanate and ferrous ammonium sulphate by a volumetric procedure using iodine monochloride as a catalyst and preoxidiser, and chloroform as indicator. Spacu and Teodorescu (*Bul. inst. Politch Bucuresti*, 1956, **18,** 47) have used chloramine-T for the indirect determination of *iso*nicotinylhydrazine.

In the present study chloramine-T has been used as an oxidant for the estimation of semicarbazide hydrochloride, benzal semicarbazone, and several substituted semicarbazones, benzoylhydrazine, benzalazine, 4-phenylsemicarbazide hydrochloride, thiosemicarbazide, phenylhydrazine hydrochloride and β-formylphenylhydrazine, using iodine monochloride-chloroform as indicator in visual titrations. Equivalence point was also determined potentiometrically in most of the titrations.

In hydrochloric acid medium each molecule of the organic derivative of hydrazine is quantitatively oxidised with chloramine-T by a four-electron change per hydrazino group:

$$N_2H_5^+ = N_2 + 5H^+ + 4\,e^-$$

## EXPERIMENTAL

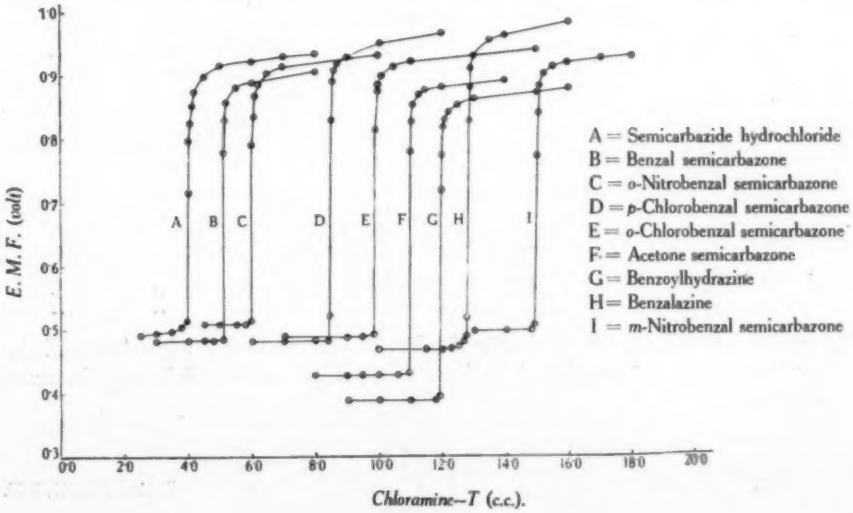
Chloramine-T was prepared according to Vogel ("Text Book of Practical Organic Chemistry", p. 822, 1948). The reagent was standardised by an iodometric method.

*Iodine Monochloride Method (Visual Titrations).*—A known amount of each substance was taken in a conical flask and water (~25 c.c.), HCl (conc., 15 c.c.), 0.02 *M* iodine monochloride (5 c.c.) and chloroform (5 c.c.) were added to it. The mixture was cooled to room temperature and titrated with a standard (0.05*M*) chloramine-T solution. The reagent was added from a burette until the solution, which was coloured with iodine, became pale yellow and chloroform layer acquired a purple colour due to iodine. The conical flask was stoppered and vigorously shaken during the titration. Addition of small volumes of chloramine-T was continued, shaking vigorously after each addition until the chloroform layer became light pale yellow due to the formation of iodine monochloride. The end-point was very sharp.

In these titrations the normality of the solution with respect to HCl was kept between 2.5*N* and 4.5*N* excepting in the cases of semicarbazide hydrochloride and 4-phenylsemicarbazide hydrochloride, where the acid normality was maintained between 0.7*N* and 1.0*N*. Several titrations were performed in each case. From the volume of the standard chloramine-T solution used, corresponding to the end-point in each titration, the amount of each substance was calculated. Some typical results are recorded in Table I.

*Potentiometric Method.*—A known amount of each substance was taken in a beaker, and water (40 c.c.) and sufficient HCl (conc.) were added to keep normality of the mixture with respect to the acid between 5.0*N* and 5.5*N*. One drop of 0.005*M* potassium iodide solution was added as a catalyst. The mixture was titrated potentiometrically with 0.05*M* chloramine-T solution.

FIG. 1



A platinum wire electrode, immersed in the solution to be titrated, was used as an oxidation-reduction electrode, and this was coupled with a saturated calomel electrode. The mixture was kept stirred with a mechanical stirrer during titration. Progress of the reaction was studied with a Mullard potentiometer. At equivalence point a sharp jump in potential was observed in each titration. A series of potentiometric titrations were performed with different amounts of each substance. The potentiometric titrations, one for each substance, are represented by curves A to I in Fig. 1.

From the volume of standard (0.05*M*) chloramine-T solution used, corresponding to the end-point in each titration, the amount of each substance was calculated. Some typical results are recorded in Table I.

TABLE I

| Organic derivatives of hydrazine. | Weight of the hydrazine derivative by Iodine monochloride method. | | Potentiometric method. | |
|---|---|---|---|---|
| | Taken. | Found. | Taken. | Found. |
| $NH_2CONH.NH_2.HCl$ | 0.0139 g.<br>0.0418 | 0.0139 g.<br>0.0417 | 0.0111 g.<br>0.0277 | 0.0111 g.<br>0.0277 |
| $C_6H_5CH{:}N.NHCONH_2$ | 0.0204<br>0.0617 | 0.0204<br>0.0615 | 0.0208<br>0.0492 | 0.0208<br>0.0491 |
| $o\text{-}NO_2C_6H_4CH{:}N.NHCONH_2$ | 0.0218<br>0.0531 | 0.0218<br>0.0529 | 0.0260<br>0.0789 | 0.0260<br>0.0791 |
| $p\text{-}ClC_6H_4CH{:}N.NHCONH_2$ | 0.0251<br>0.0748 | 0.0251<br>0.0746 | 0.0197<br>0.0591 | 0.0197<br>0.0591 |
| $o\text{-}ClC_6H_4CH{:}N.NHCONH_2$ | 0.0247<br>0.0752 | 0.0247<br>0.0750 | 0.0242<br>0.0738 | 0.0242<br>0.0736 |
| $(CH_3)_2C{:}N.NHCONH_2$ | 0.0142<br>0.0433 | 0.0142<br>0.0432 | 0.0147<br>0.0425 | 0.0147<br>0.0424 |
| $C_6H_5CONH.NH_2$ | 0.0173<br>0.0509 | 0.0173<br>0.0508 | 0.0173<br>0.0433 | 0.0173<br>0.0432 |
| $(C_6H_5CH{:}N\text{-})_2$ | 0.0208<br>0.0640 | 0.0208<br>0.0638 | 0.0207<br>0.0667 | 0.0207<br>0.0668 |
| $m\text{-}NO_2C_6H_4CH{:}N.NHCONH_2$ | 0.0263<br>0.0759 | 0.0263<br>0.0757 | 0.0257<br>0.0782 | 0.0257<br>0.0780 |
| $C_6H_5NHCONH.NH_2$ | 0.0234<br>0.0610 | 0.0234<br>0.0609 | ..<br>.. | ..<br>.. |
| $NH_2CS.NH.NH_2$ | 0.0091<br>0.0228 | 0.0091<br>0.0228 | ..<br>.. | ..<br>.. |
| $o\text{-}HO.C_6H_4CH{:}N.NHCONH_2$ | 0.0225<br>0.0669 | 0.0225<br>0.0667 | ..<br>.. | ..<br>.. |
| $p\text{-}CH_3OC_6H_4CH{:}N.NHCONH_2$ | 0.0254<br>0.0741 | 0.0254<br>0.0739 | ..<br>.. | ..<br>.. |
| $C_6H_5NH.NH_2.HCl$ | 0.0181<br>0.0447 | 0.0181<br>0.0446 | ..<br>.. | ..<br>.. |
| $H.CONH.NH.C_6HN_5$ | 0.0173<br>0.0515 | 0.0173<br>0.0513 | ..<br>.. | ..<br>.. |

The results recorded above show that the listed reductants can be determined volumetrically by titrating with a standard chloramine-T solution. All chemicals used in this investigation are of guaranteed purity.

DEPARTMENT OF CHEMISTRY,
PANJAB UNIVERSITY, CHANDIGARH.

*Received April* 11, 1960.

[Jour. Indian Chem. Soc., Vol. 37, No. 7, 1960]

# CATION EXCHANGE BETWEEN COLLOIDAL CLAYS AND RESINS IN WATER AND AQUEOUS ALCOHOL AS A FUNCTION OF THE CONCENTRATION OF THE DISPERSED PHASE

By Amalesh Chatterjee

Exchange studies have been made between varying amounts of H-resins and varying concentrations of clays saturated with $NH_4$, Mg and Ba ions. The amounts of hydrogen ions from the resin exchanged for the cations of the clays have been determined by titrating with an alkali. Experiments with the varying amounts of H-resin yield isotherms which are more or less similar in shape to ordinary adsorption isotherms in the case of Mg- and Ba- clays, but the slope is somewhat linear in the case of ammonium clay. The exchange of ions usually decreases with the concentration of the clay suspension.

Experiments have been carried out in aqueous as well as in aqueous-alcohol media, and the results interpreted in terms of the hydration of cations and on the basis of the concept that exchange takes place by an overlapping of the double layers of the two solid phases.

The immediate object of the work presented here is to evaluate the behaviour of exchangeable cations present in soil or clay towards a solid exchanging material. The ultimate aim is to use it as a basis for interpreting soil-plant root relationships. It is assumed that plant roots can adsorb ions from the surrounding soil by a process of ion exchange. But the procedure by which the exchange property of clays is generally studied is, more or less, arbitrary and little simulates the conditions obtaining in the plant-root zone. For instance, the exchange of ions is usually studied in dilute systems, and that too in presence of, perhaps, foreign electrolytes at a concentration quite inconceivable in the root zone. The usual practice is to extrapolate or apply, as it is, the information gained under the artificial conditions to the natural soil-root system. Brown and Albrecht (Res. Bull. No. 477, College of Agric., Univ. of Mo., 1950) recognised this artificiality and studied the exchange property of soils under conditions which simulated, more or less, those obtaining in the soil-root system. Their technique consisted in having a hydrogen system (clay or the plant root) separated by a suitable semipermeable membrane (collodion or cellophane) from the soil colloid, saturated with one or more kinds of ions. The membrane did not seem to prevent exchange and, what was more important, the soil-root conditions were simulated. Chatterjee (*J. Indian Soc. Soil Sci.*, 1954, **2**) also carried out experiments with H-resin, simulating plant roots, which were kept in cellophane bags, and thus separated from the soil colloid which was saturated with sodium, potassium and calcium ions, separately. The present work is an extension of this work (*loc. cit.*) with clays having exchangeable ammonium, magnesium and barium ions.

The ease of replacement of cations is known to depend on their size and degree of hydration. It is also known that in ethanol, in which the ions would be hydrated much less, if at all, the usual lyotropic series is reversed, so that ions are held in the order of their true ionic size and not in the order of their hydrated size. In order therefore to ascertain the role of ionic hydration in the exchange of the cations, experiments have also been carried out in aqueous ethanolic media.

## EXPERIMENTAL

Known amounts of the H-resin were taken inside a small cellophane bag, fastened at the end of a pyrex tube, and moistened with water. It was then immersed into suspensions of base-saturated clays or clay salts of varying concentration, contained in a beaker. The contents were covered by paraffin sealing in order to prevent evaporation of water from the beaker. The system was allowed to remain in this condition with occasional cautious shaking, and the *p*H of the clay suspension in the beaker was measured from time to time with a glass electrode till it became constant. The equilibrium was usually attained within 5 days, but the arrangement was not dislodged before 7 to 10 days. The amount of exchangeable hydrogen in the clay suspension was then determined by titration with KOH in presence of KCl (Ganguly, *J. Phys. Coll. Chem.*, 1951, **55**, 1417). This is equivalent to the amount of cation of the base-saturated clay which has been exchanged for the H-ions of the resin.

The amount of H-resin was varied in such a manner that the total amounts of hydrogen ion associated with it corresponded to 0.5 S, 1.0 S, 1.5 S and 2.0 S respectively where, S is the symmetry concentration. Results shown graphically in Figs. 1-3 record the variation of amounts of cation exchanged for the hydrogen of the H-resin with the concentration of the base-saturated clay suspension, and with the symmetry concentration of the hydrogen ions.

Three series of experiments were performed with ammonium, magnesium and barium clays in aqueous medium, in 30% and 50% ethanol. The base-saturated clays were prepared from Padegaon B type clay, which is a montmorillonite.

## DISCUSSION

Sections (*a*) of the figures represent the amount of cation exchanged as a function of the symmetry concentration of the hydrogen ions in the H-resin, and sections (*b*) represent the amount of cation exchanged as a function of the concentration of the clay salt which is set against a definite amount of the H-resin.

The influence of the concentration of the clay on the ease of replacement of the cation saturating it for the hydrogen ion of the H-resin is clearly noticeable from the graphs in figures (*b*). Each cation appears to have its characteristic case of exchange. In the case of the three cations studied here, the replacement is greatly hindered at high concentrations. This is much more prominent in the case of systems in which larger amounts of resin were used.

Figures (*a*) are similar to the usual exchange isotherms. The graphs for magnesium and barium clays have more or less the same form. The same for ammonium clay are somewhat more linear.

The decrease in the ease of replacement with the increasing concentration of the clay, as is particularly evident in case of the divalent clays, is most probably caused by the overlapping of the electrical double layers of the clay particles, thereby causing an "immobilisation" of the ions (Chatterjee, *loc. cit.*).

In the case of the ammonium clay, the effect of concentration of the clays or of hydration on the exchange of ammonium ion is limited to the low concentration region (near about 2.5%), above which the exchangeability changes very little. The double layers associated with the clay particles appear to have come closest at a concentration of about 2.5%.

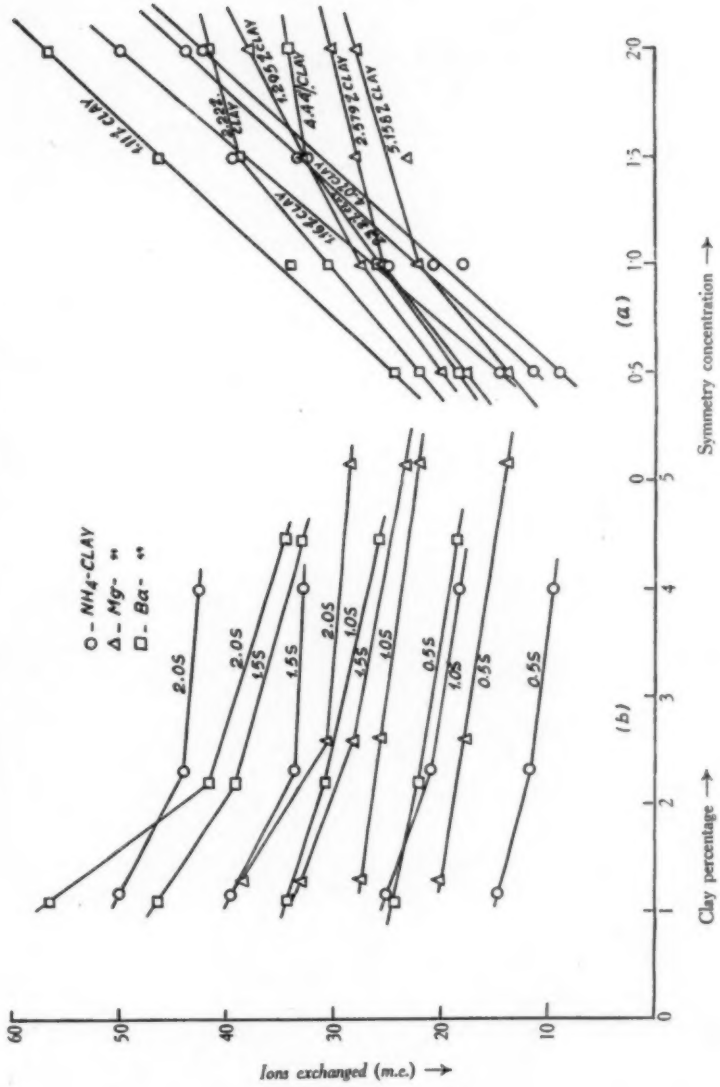



FIG. 1

*Exchange characteristics of cations in aqueous medium.*

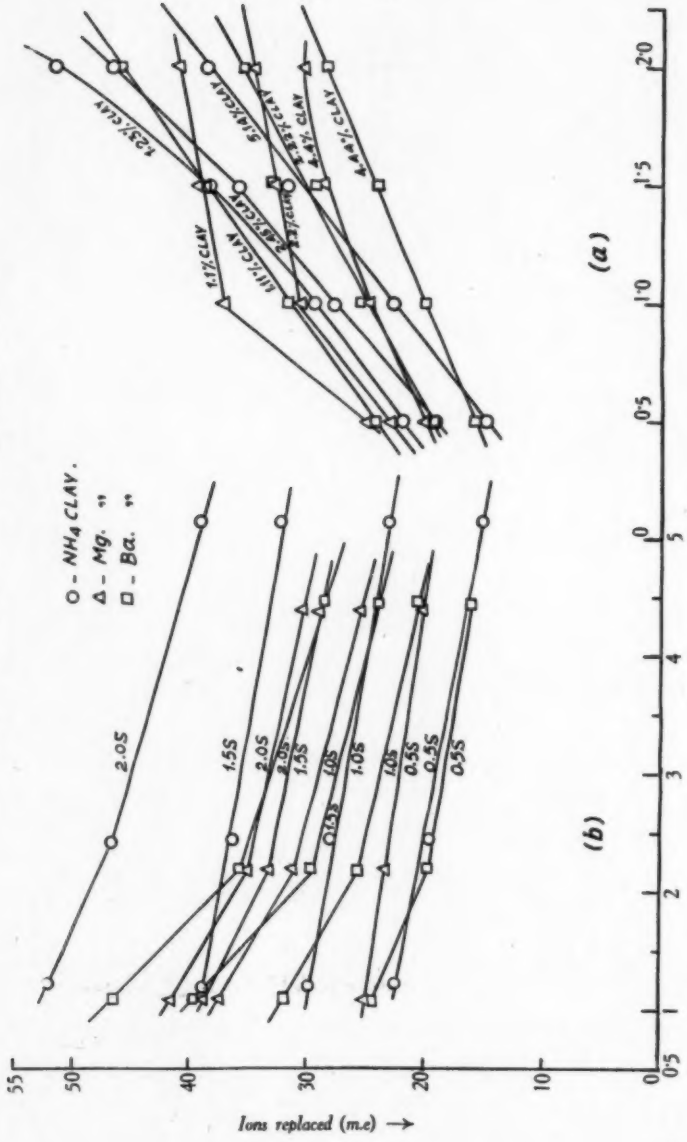



FIG. 2

*Exchange characteristics of cations in 30% ethanolic medium.*

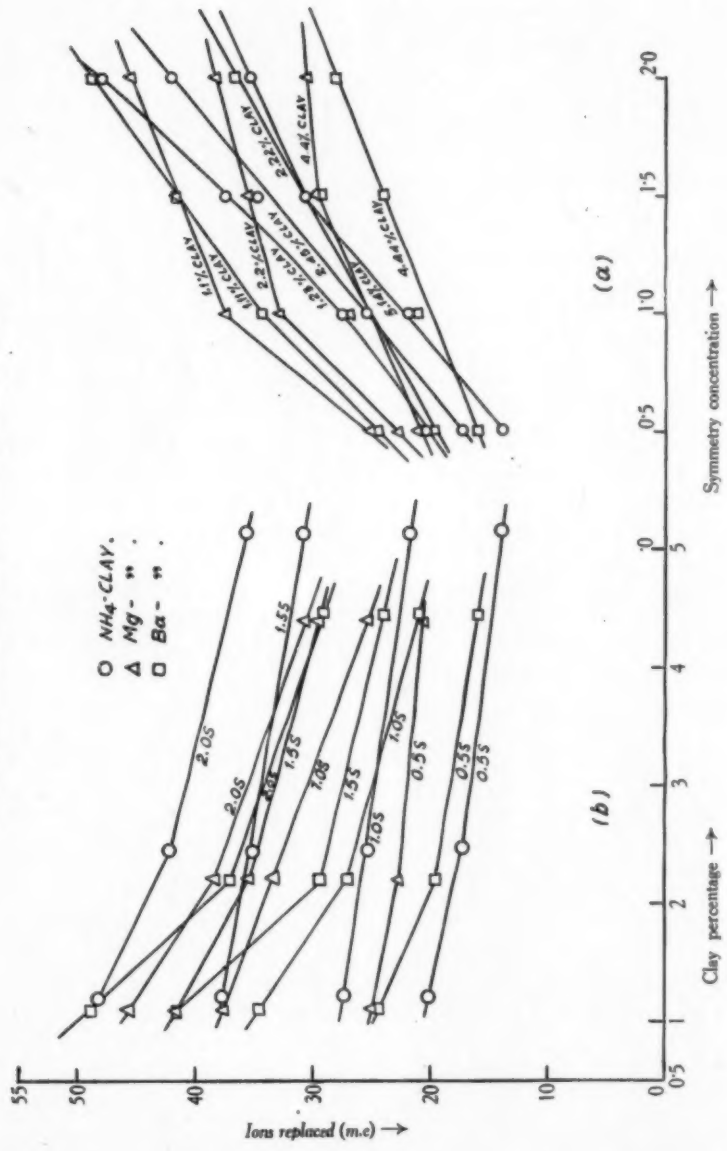



FIG. 3

*Exchange characteristics of cations in 50% ethanolic medium.*

Figures 2 and 3 show the exchange characteristics of the ions in aqueous ethanol media having 30% and 50% ethanol. It will be observed from Figs. 2 and 3 that the variation in the % exchange with the concentration of either clay or the amount of H-resin follows a more or less similar trend, viz., the % exchange decreases very sharply for the base-saturated clays as the concentration of clay increases; it increases in some cases nearly linearly, and in others according to the usual exchange isotherms, as the amount of the exchanging H-resin is increased. Apart from this trend, there is a distinct difference from a similar exchange study carried out in purely aqueous media. The decrease in the exchange of cations as the clay concentration increases, is much greater in water-ethanol medium than in water alone. Similarly, the release of the cations from the clays against hydrogen ions of the resins is considerably reduced in presence of ethanol, *i.e.*, the exchange isotherms of the clay-resin system have a flatter run.

Two factors which are likely to influence exchange in presence of ethanol may be considered. As a result of dehydration caused by ethanol, the double layers of contiguous particles overlap and the exchangeable cations are "immobilised"; so to say, this tends to lower the exchangeability as the graphs show. A similar feature is observed in the case of clay salts in purely aqueous medium when the concentration is high. The other factor, besides dehydration, which is likely to influence exchange in presence of ethanol may be the decrease in the dielectric constant and a consequent lowering of activity and a decreased exchangeability.

Sincere thanks of the author are due to Dr. S. K. Mukherjee, UNESCO Consultant and Professor of Chemistry, for his valuable suggestions and continued interest in the progress of the work and for providing laboratory facilities.

Department of Applied Chemistry,
University Colleges of Science &
Technology, Calcutta.

*Received February* 15, 1960.

[Jour. Indian Chem. Soc., Vol. 37, No. 7, 1960]

# INTERACTION OF CHARCOAL WITH IODINE IN AQUEOUS SOLUTION

By Balwant Rai Puri and D. D. Singh

The interaction of charcoal with iodine in aqueous solution under different conditions has been studied in some details. The amount of iodine removed from solution by charcoal under standard conditions is influenced considerably by the nature of the charcoal surface. Such determinations therefore cannot be used for measuring surface areas of charcoal. An appreciable fraction of the iodine removed from solution is, in fact, converted into hydriodic acid, the corresponding amount of oxygen being chemisorbed by the charcoal, giving rise to $CO_x$-complex. While a small amount of iodine is adsorbed reversibly by all types of charcoals, another small amount is adsorbed irreversibly by degassed charcoals only.

It appears from the literature that the results obtained by several workers on the adsorption of iodine by charcoals and carbon blacks (Herz and Lorenz, *Kolloid Z.*, 1929, **47,** 331; Smith *et al.*, *Ind. Eng. Chem.*, 1941, **33,** 1303; Watson and Parkins, *ibid.*, 1955, **47,** 1053; King, *J. Chem. Soc.*, 1937, 1489; Linner and Willman, *J. Phys. Chem.*, 1950, **54,** 605; Razouk and Shimi, *A'in Shams. Sci. Bull.*, 1953, **2,** 203) are often at variance with one another. Smith *et al.* as well as King, and Linner and Willman have attempted to correlate iodine adsorption with surface area of the adsorbent, but the work of Watson and Parkins as well as that of Razouk and Shimi does not appear to confirm this conclusion.

The importance of measuring iodine adsorption under fixed conditions, such as, pretreatment of the adsorbent, the amount of the adsorbent used, initial concentration and quantity of the iodine solution used, ratio of $KI/I_2$ in the solution, time of contact, etc. has been rightly emphasised by Koide *et al.* (*J. Soc. Rubber Ind., Japan*, 1950, **23,** 111). It was thought of interest to study the adsorption of iodine from aqueous solution by different samples of charcoal under standardised conditions and to gain an insight into the mechanism involved about which very little appears to have been reported so far.

## Experimental

Two samples of charcoal, prepared by the carbonisation of cane-sugar and coconut shells, as described earlier (Puri *et al.*, this *Journal*, 1958, **35,** 181), were used before as well as after degassing at 750° and 1200°. The surface areas of these samples were calculated from their water isotherms (Puri *et al.*, *ibid.*, 1952, **29,** 841) by using Harvey's calculations (*J. Amer. Chem. Soc.*, 1943, **65,** 2343).

Iodine solutions of concentrations varying from 0.05 to 0.30*N* were prepared in potassium iodide solutions of different concentrations.

*Procedure.*—One g. portions of each charcoal were mixed with 100 c.c. of the various iodine solutions. The suspensions were shaken mechanically in half-pound bottles, wrapped in thick black papers, for different intervals of time after which an aliquot of the clear supernatant liquid was examined for unchanged iodine and hydriodic acid formed, if any, by the usual analytical methods. The results of blanks did not show any fall in the concentration of iodine solutions under similar conditions.

Two g. portions of the various samples of charcoal (oven-dried at 110°) before as well as after treatment with iodine solution under optimum conditions were subjected to evacuation at 1200° in a resistance tube furnace and the gases evolved were analysed in an Orsat-Lunge gas analysis apparatus, as described before (Puri *et al.*, *loc. cit.*, 1958).

The *p*H values of the charcoal suspensions (1:5) were determined by using a Cambridge glass electrode *p*H meter.

The base-adsorption capacity (b.a.c.) was determined by shaking 1 g. charcoal with 100 c.c. of 0.2 *N* barium hydroxide solution for 48 hours and titrating an aliquot of the clear supernatant liquid against a standard acid solution in the usual way.

TABLE I

*Amounts of iodine adsorbed by original sugar charcoal after shaking for 24 hours.*

| $KI/I_2$ ratio. | Amount adsorbed (m.e./g.) when the concentration of the solution is: | | | | | |
|---|---|---|---|---|---|---|
| | 0.05 *N*. | 0.10 *N*. | 0.15 *N*. | 0.20 *N*. | 0.25 *N*. | 0.30 *N*. |
| 3 : 1 | 3.10 | 3.40 | 4.30 | 4.85 | 5.00 | 5.03 |
| 4 : 1 | 2.50 | 3.60 | 3.68 | 3.85 | 4.05 | 4.05 |
| 5 : 1 | 2.00 | 2.65 | 2.90 | 3.30 | 3.55 | 3.59 |
| 6 : 1 | 1.90 | 2.15 | 2.58 | 2.80 | 3.15 | 3.12 |

## DISCUSSION

It is evident from the results recorded in Table I that, for a given $KI/I_2$ ratio, the magnitude of adsorption increases with increase in the concentration of the solution and that the value becomes almost constant when the concentration is 0.25 *N*. It is also evident that the intensity of adsorption is influenced considerably by the amount of potassium iodide in the solution, and that for a given concentration of iodine solution, it increases with decrease in the $KI/I_2$ ratio. It appears that for maximum adsorption this ratio should not exceed 3:1. It was not convenient to prepare iodine solution of moderate concentrations in which this ratio was less than 3.

TABLE II

*Effect of time of shaking on the adsorption of iodine by original sugar charcoal from a 0.25 N iodine soln. containing 3 moles of* KI *per mole of iodine.*

| Shaking time (hrs.) | 2 | 4 | 6 | 8 | 12 | 24 | 48 | 96 |
|---|---|---|---|---|---|---|---|---|
| Iodine adsorbed (m.e./g.) | 2.20 | 2.95 | 3.51 | 3.90 | 4.39 | 5.05 | 5.12 | 5.10 |

It is seen (Table II) that mechanical shaking for a minimum period of 24 hours is necessary for the attainment of equilibrium when maximum value is obtained.

In all subsequent experiments 1 g. charcoal was mixed with 100 c.c. of freshly prepared 0.25*N* iodine solution containing 3 moles of potassium iodide per mole of iodine, and the suspension was shaken mechanically for about 24 hours.

The amounts of iodine adsorbed by the various samples of charcoal under these conditions are recorded in Table III. The surface areas of the adsorbents are also included. It is seen that neither sugar charcoal nor coconut-shell charcoal undergoes any noticeable decrease in surface area on evacuation. This is consistent with the previous observation of some other workers as well (Emmett and Anderson, *J. Amer. Chem. Soc.*, 1945, **67**, 1492; McDermot and Arnell, *J. Phys. Chem.*, 1954, **58**, 492). However, iodine adsorption by each charcoal undergoes a considerable decrease on evacuation. It appears therefore that iodine adsorption is considerably influenced by the *nature* of the charcoal surface.

TABLE III

*Iodine adsorption, surface area and pH values of the various samples of charcoal.*

| Samples. | Iodine adsorbed (m.e./g.). | Surface area ($m^2$./g.). | pH value. |
|---|---|---|---|
| Sugar charcoal : | | | |
| Original | 5.10 | 425 | 2.85 |
| 750°-evacuated | 3.75 | 420 | 6.98 |
| 1200°-evacuated | 2.60 | 423 | 8.80 |
| Coconut-shell charcoal : | | | |
| Original | 3.80 | 361 | 3.38 |
| 750°-evacuated | 2.91 | 362 | 6.90 |
| 1200°-evacuated | 2.12 | 359 | 8.37 |

The *p*H values of the water suspensions of the various samples of charcoal are also included in Table III. It is seen that the original samples have fairly low and the degassed samples have fairly high *p*H values. It appears therefore that a low *p*H favours and a high *p*H hinders the adsorption of iodine. Thus adsorption of iodine does not provide a suitable method for estimating surface areas of carbons as considered by some workers (*loc. cit.*).

*Mechanism of Iodine Adsorption by Charcoal.*—To ascertain the mechanism involved in the adsorption of iodine from aqueous solution by charcoal, the supernatant liquid, after shaking 1 g. portions of the various samples with 100 c.c. of 0.25 *N* iodine solution, was carefully analysed for iodine left unchanged and for hydriodic acid formed. The charcoal, after the treatment, was thoroughly washed, first with water and then with $CCl_4$ to remove the reversibly adsorbed iodine. It was then dried at 110° in an air-oven and subjected to evacuation at 1200° to find out the amount of oxygen chemisorbed, if any, during the process. The gaseous mixture above each reaction bottle was also analysed to see if any oxygen or oxides of carbon were formed during the process, but there were none.

TABLE IV

*Account of iodine removed from solution after interaction with charcoal together with increase in oxygen content of the sample.*

| Samples. | Iodine added. | Iodine removed from soln. | HI formed. | Iodine recovered on washing (reversibly adsorbed). | Iodine adsorbed irreversibly (by diff.). | Iodine recovered on evacuation at 1200°. | Increase in $O_2$ content evolved as $CO_2$. |
|---|---|---|---|---|---|---|---|
| | | | (Results are expressed in m.e./g.) | | | | |
| Sugar charcoal : | | | | | | | |
| Original | 25.00 | 5.00 | 4.07 | 0.93 | Nil | Nil | 4.00 |
| 750°-evacuated | 25.00 | 3.80 | 2.75 | 0.60 | 0.45 | 0.38 | 2.70 |
| 1200°-evacuated | 25.00 | 2.71 | 1.80 | 0.56 | 0.35 | 0.36 | 1.78 |
| Coconut-shell charcoal : | | | | | | | |
| Original | 25.00 | 3.85 | 3.23 | 0.62 | Nil | Nil | 3.12 |
| 750°-evacuated | 25.00 | 2.95 | 2.05 | 0.50 | 0.40 | 0.32 | 2.08 |
| 1200°-evacuated | 25.00 | 2.20 | 1.48 | 0.35 | 0.37 | 0.35 | 1.50 |

The results of these experiments are recorded in Table IV. It is seen, in the first instance, that an appreciable proportion of the amount of iodine removed from solution (col. 3), which has been usually attributed to 'adsorption', actually represents the amount converted into hydriodic acid (col. 4), presumably by the hydrolysis of iodine brought about in the presence of charcoal. The amount of oxygen evolved in the reaction appears to be chemisorbed by the charcoal as there

is a considerable increase in the amount of $CO_2$ evolved on degassing each sample after the treatment (Table V). This increase, calculated as oxygen (col. 8, Table IV) is seen to be almost exactly equivalent to the amount of HI formed (col. 4).

It may be mentioned that there was no increase in the amount of $CO_2$ or $H_2O$ evolved from any sample of charcoal after the treatment. This shows that the oxygen chemisorbed by the charcoal during the process gives rise to $CO_2$-complex only.

TABLE V

*B.a.c. of charcoal in relation to $CO_2$ evolved on evacuation at 1200° before and after treatment with iodine soln.*

(Results are expressed in m.e./100g.)

| Samples. | $Ba(OH)_2$ neutralised. | $CO_2$ evolved on evacuation. | $Ba(OH)_2$ neutralised. | $CO_2$ evolved on evacuation. |
|---|---|---|---|---|
| | Before treatment. | | After treatment. | |
| Sugar charcoal : | | | | |
| Original | 677.82 m.e./g. | 686.40 m.e./g. | 880.50 m. | 886.40 |
| 750°-evacuated | Nil | Nil | 59.88 | 135.05 |
| 1200°-evacuated | Nil | Nil | 35.25 | 88.99 |
| Coconut-shell charcoal : | | | | |
| Original | 312.45 | 317.00 | 466.95 | 472.05 |
| 750°-evacuated | Nil | Nil | 49.46 | 104.10 |
| 1200°-evacuated | Nil | Nil | 30.25 | 75.00 |

It is seen (Table IV) that while in case of the original samples, the entire amount of iodine removed from solution (col. 3) can be accounted for as hydriodic acid formed (col. 4) and iodine adsorbed physically or reversibly (col. 5) in case of the evacuated samples, a small amount of iodine remains unaccounted for. It appears therefore that unlike the original samples, the evacuated samples can fix a small amount of iodine irreversibly which probably becomes fixed at some unsaturated sites created by the elimination of the chemisorbed gases during the preliminary high temperature evacuation treatment. Small portions (about 1 g.) of these samples, after the treatment with iodine, were degassed at 1200° in a separate experiment to find out whether any of the 'fixed' iodine was eliminated at this temperature. The gases evolved were passed through a solution of potassium iodide which was titrated afterwards against a standard sodium thiosulphate solution in the usual way. The amount of iodine, thus recovered, is shown in column 7 and is seen to be fairly close to the amount which could not be accounted for (col. 6).

It is evident from the results recorded herein that not only the magnitude of the so-called 'adsorption' of iodine from aqueous solution by charcoal but even the course of the reactions involved are largely influenced by the *nature* of the charcoal surface.

The amounts of barium hydroxide neutralised and the amounts of $CO_2$ evolved on degassing at 1200° in case of the various samples of charcoal are recorded in Table V. It is seen that both the values increase as a result of the treatment with iodine solution. However, the two values are in close agreement only in case of the original samples. In the evacuated samples the amount of alkali neutralised is considerably less than the amount of $CO_2$ evolved. This shows that the $CO_2$-complex formed on evacuated charcoal by iodine treatment differs from that formed in original charcoal in as much as it is not completely titratable against alkalies.

CHEMISTRY DEPARTMENT,
PUNJAB UNIVERSITY,
HOSHIARPUR.

*Received April* 11, 1960.

[Jour. Indian Chem. Soc., Vol. 37, No. 7, 1960]

# INVESTIGATIONS ON THE REDUCTION OF MERCURIC CHLORIDE BY OXALIC ACID INDUCED BY POTASSIUM PERSULPHATE

BY L. K. SAXENA AND C. P. SINGHAL

The kinetics of the reduction of mercuric chloride has been studied at various temperatures and concentrations of the reactants. The reaction is found to progress through various zones such as : (*i*) period of induction, (*ii*) normal reaction of zero order, (*iii*) auto-catalysis, (*iv*) auto-inhibition and (*v*) reversible reaction. A tentative mathematical expression, based on the chain mechanism of the reaction, has been derived for the velocity of reduction of mercuric chloride. Sodium acetate up to a limiting concentration is found to accelerate the reduction tremendously, but it produces an inhibiting influence when in large excess.

The activation of oxalic acid in presence of oxidising agents, such as potassium permanganate, potassium persulphate, etc., manifested in the ready reduction of mercuric chloride to mercurous state, was first observed by Dhar (*J. Chem. Soc.*, 1917, **111,** 690; this *Journal*, 1928, **5,** 203) and subsequently studied by Oberhauser *et al.* (*Ber.*, 1928, **61,** 521; *Annalen*, 1929, **470,** 111) and others (Wieland and Zilg, *Annalen*, 1937, **530,** 257; Thunberg, *Arch. Physiol.*, 1928, **54,** 6; Abel, *Z. Elektrochem.*, 1937, **43,** 629). Weiss (*Trans. Faraday Soc.*, Disc., 1947, **2,** 188) suggested a chain mechanism based on the formation of $C_2O_4^-$ radical in the oxidation of oxalic acid by potassium permanganate to explain the reduction of mercuric chloride by oxalic acid-permanganate system. Ladbury and Cullis (*Chem. Rev.*, 1958, **58,** 403) and Waters (*Quart. Reports*, 1959) have discussed the postuation of free radicals, such as $CO_2^-$, and their relevant role in similar mechanisms of redox reactions. Prasad and Bhattacharya (this *Journal*, 1956, **33,** 3) studied this reaction from the view point of the concentration effect of the inductor (potassium permanganate) on the induction period and extent of reduction of mercuric chloride.

The induced reduction of mercuric chloride by oxalic acid in presence of potassium persulphate was quantitatively studied by Dhar (*loc. cit.*) who observed the relationship between the amount of inductor used and the amount of calomel formed. The present investigation includes the kinetics of the reduction of mercuric chloride by oxalic acid induced by potassium persulphate, and an attempt has been made to explain the mechanism of this reduction.

## EXPERIMENTAL

The experimental procedure was the same as described in a subsequent part (under publication). For studying the kinetics, the reaction was allowed to progress for different intervals of time in different conical flasks under identical conditions of temperature and concentrations of the reactants. The amount of calomel precipitated in each flask at desired intervals of time was filtered off through a double-walled funnel containing ice-cold water in between its walls. This prevented further reduction of mercuric chloride even during filtration. The precipitate was then washed and estimated by a standard potassium iodate solution (Vogel, "Text Book of Quantitative Inorganic Analysis", pp. 361-367). The influence of nitrogen and sodium acetate on the kinetics of the reduction of mercuric chloride was also studied. The zero-order velocity constant was calculated by the expression :

$$k_0 = dc/dt$$

where $dc$ is the amount of mercurous chloride (in terms of $KIO_3$) formed during an interval $dt$.

### *Influence of Temperature*

The reaction was studied at different temperatures. The results obtained at 50° are summarised in Table I and the influence of temperature on this reaction is represented by Fig. 1.

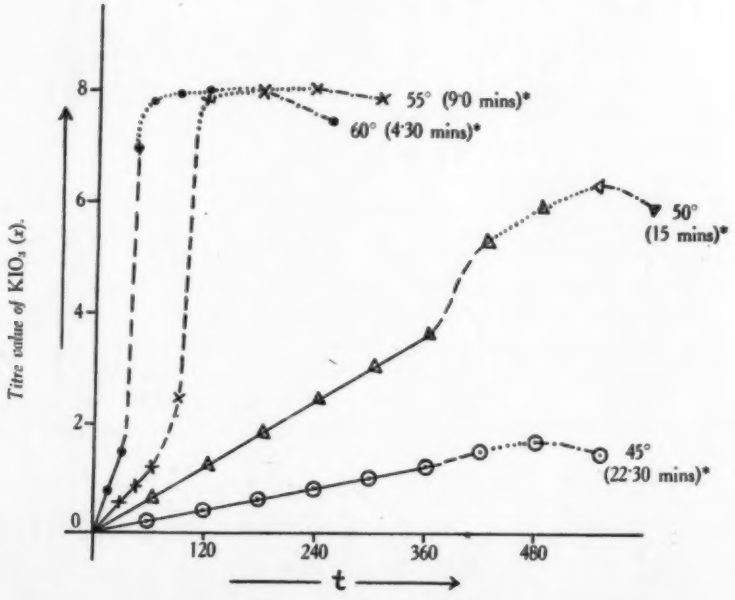
TABLE I

$(K_2S_2O_8)_0 = (H_2C_2O_4)_0 = (HgCl_2)_0 = 0.02\ M$. Temp. = 50°. Period of induction = 15.0 mins.

| Time ($t$). | Volume of $KIO_3$. | Average $C$. | $k_0 \times 10^3$. |
|---|---|---|---|
| 0 min. | 0.0 c.c. | 20.0 | .. |
| 60 | 0.6 | 19.7 | 10.00 |
| 120 | 1.2 | 19.1 | 10.00 |
| 180 | 1.8 | 18.5 | 10.00 |
| 240 | 2.4 | 17.9 | 10.00 |
| 300 | 3.0 | 17.3 | 10.00 |
| 360 | 3.6 | 16.7 | 10.00 |
| 420 | 5.2 | 15.6 | 26.66 |
| 480 | 5.8 | 14.5 | 10.00 |
| 540 | 6.3 | 13.95 | 8.33 |
| 600 | 4.8 | 14.45 | −25.00 |

From Table I and Fig. 1, it is observed that at 50° the reaction after a period of induction slowly develops, exhibiting zero-order for 360 mins. After this period the velocity abruptly increases up to 420 mins., and then diminishes gradually. At 600 mins. the value of $k_0$ is found to be negative, suggesting the reversibility of the reaction. These observations lead to the

FIG. 1



conclusion that the whole course of the reaction consists of five zones: (*i*) Period of induction, (*ii*) normal reaction, (*iii*) auto-catalysis, (*iv*) auto-inhibition and (*v*) reversible reaction, and may be governed by a chain mechanism.

From Fig. 1 it may be seen that an increase of temperature increases the velocity of the overall reaction and affects its various zones. The periods of induction and normal velocity decrease, while the rate of auto-catalysis increases and its period is shifted towards earlier intervals. Both, the period of auto-inhibition and the stage of reversibility, set in earlier. The temperature coefficient of the reaction during its normal course is found to be 5.9 between 45° and 55° and 5.4 between 50° and 60°. The corresponding activation energies are 36,780 and 36,100 cals. An interesting feature of the reaction is that the reduction of mercuric chloride does not proceed to completion. The maximum reduction at 60° is about 40%.

### *Influence of Concentrations of Reactants*

Table II records the results of six sets of experiments showing the influence of concentration of the reactants on the values of zero-order velocity constant. In each set the concentrations of two reactants were kept equal to 0.02 *M*, and the third was varied as noted in the columns.

TABLE II

Temperature = 50°.

| *t*. | $(K_2S_2O_8)_0=(HgCl_2)_0=0.02M$. With $(H_2C_2O_4)_0$ | | $(K_2S_2O_8)_0=(H_2C_2O_4)_0=0.02M$. With $(HgCl_2)_0$ | | $(H_2C_2O_4)_0=(HgCl_2)_0=0.02M$. With $(K_2S_2O_8)_0$ | |
|---|---|---|---|---|---|---|
| | $k_0\times10^3$ | | $k_0\times10^3$ | | $k_0\times10^3$ | |
| | 0.04 *M*. | 0.08 *M*. | 0.04 *M*. | 0.08 *M*. | 0.04 *M*. | 0.08 *M*. |
| 0 min. | .. | .. | .. | .. | .. | .. |
| 60 | 11.66 | 13.33 | 13.33 | 21.66 | 13.33 | 20.00 |
| 120 | 10.00 | 10.00 | 13.33 | 20.00 | 25.00 | 26.66 |
| 180 | 10.00 | 11.66 | 12.50 | 21.66 | 35.00 | —1.66 |
| 240 | 10.00 | 11.66 | 15.83 | 26.66 | 3.33 | —1.66 |
| 300 | 16.66 | 33.33 | 21.66 | 38.33 | —1.66 | —1.66 |

From Tables I and II it is observed that the zero-order velocity constant is not appreciably affected by increasing the concentration of oxalic acid. This suggests that the order of the reaction with respect to oxalic acid is zero. It also appears that $k_0$ increases with increase in the concentration of mercuric chloride. The order of the reaction with respect to mercuric chloride, calculated from the data of these tables by the differential method, is found to change from 0.5 to 1.0 with the progress of the reaction. By increasing the concentration of potassium persulphate, the zero-order velocity constant does not show constancy as the reaction becomes auto-catalytic sooner, but auto-inhibition and reversibility set in earlier. Hence, it is difficult to assign any definite order of the reaction with respect to potassium persulphate. The maximum reduction of mercuric chloride decreases by increasing the concentration of persulphate.

### *Influence of Nitrogen*

To study the influence of nitrogen on the reduction of mercuric chloride, nitrogen gas was bubbled through the reaction mixture at a uniform rate. The results are recorded in Table III.

TABLE III

$(K_2S_2O_8)_0 = (H_2C_2O_4)_0 = (HgCl_2)_0 = 0.02\ M$. Temp. = 50°.

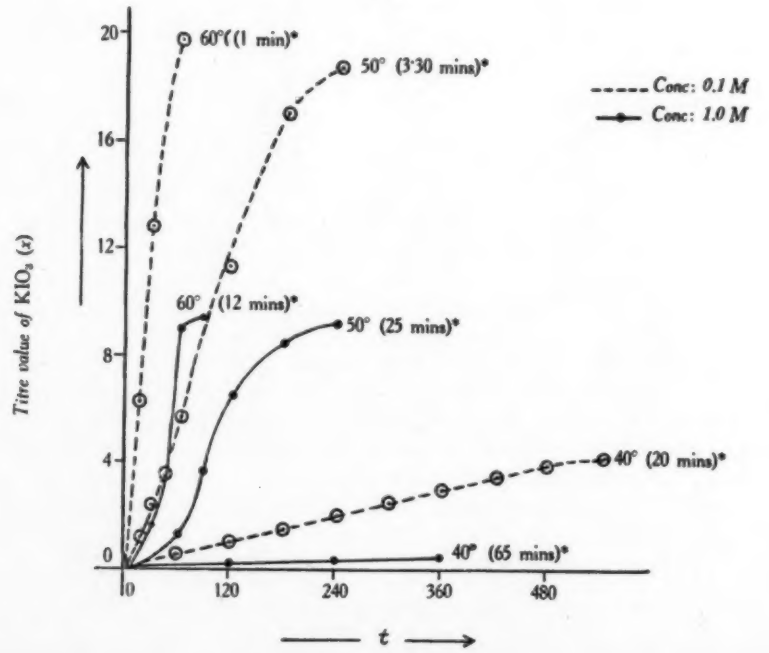
| $t$. | Volume of $KIO_3$. | Average $C$. | $k_0 \times 10^3$. |
|---|---|---|---|
| 0 min. | 0.0 c.c. | 20.0 | .. |
| 30 | 2.0 | 19.0 | 66.666 |
| 60 | 4.0 | 17.0 | 66.666 |
| 120 | 8.8 | 13.6 | 80.000 |
| 180 | 9.6 | 10.8 | 13.333 |
| 240 | 9.3 | 16.6 | −5.000 |

Comparing Table III with Table I, it may be seen that nitrogen exerts an accelerating influence on the velocity of formation of mercurous chloride. The reduction of mercuric chloride reaches up to about 50%.

*Influence of Sodium Acetate*

The reduction of mercuric chloride was studied at 40°, 50° and 60° in presence of two different concentrations of sodium acetate, keeping the concentration of each of the reactants and the inductor equal to 0.02 *M*. The results obtained are represented in Fig. 2. On comparing it with Fig. 1, it is observed that in presence of 0.1 *M* sodium acetate, the period of normal velocity at 50° and 60° decreases with increase of temperature and auto-catalysis, followed by auto-inhibition, set

FIG. 2




*Period of induction.*

in earlier. However, reversibility of the reaction is not observed and the overall reaction is much faster than that without sodium acetate. The reduction of mercuric chloride goes to almost completion in one hour at 60°. It is further noted that on increasing the concentration of the acetate to 1.0 *M*, the velocity of reduction of mercuric chloride is suppressed, but yet remains higher than that without the acetate (cf. Figs. 1 & 2). It is interesting to note that in presence of 0.1 *M* sodium acetate, the period of induction observed is much less than that without it, but when the concentration of the acetate is 1.0 *M*, this period becomes larger than that when no sodium acetate is used.

## DISCUSSION

Investigation of the kinetics of the reduction of mercuric chloride reveals that the reaction develops through various zones and may be governed by a chain mechanism as shown below :

$$S_2O_8^{2-} \longrightarrow 2\,SO_4^- \qquad \text{slow} \qquad (1)$$

$$SO_4^- + C_2O_4^{2-} \longrightarrow SO_4^{2-} + CO_2^- + CO_2 \qquad \text{fast} \qquad (2)$$

$$CO_2^- + S_2O_8^{2-} \longrightarrow SO_4^{2-} + SO_4^- + CO_2 \qquad ,, \qquad (3)$$

$$CO_2^- + Hg^{2+} \longrightarrow CO_2 + Hg^+ \qquad \text{(faster than step 3)} \qquad (4)$$

$$Hg^+ + C_2O_4^{2-} \longrightarrow Hg + CO_2^- + CO_2 \qquad \text{fast} \qquad (5)$$

$$Hg + Hg^{2+} \longrightarrow Hg_2^{2+} \qquad ,, \qquad (6)$$

Chain breaking processes :—

$$SO_4^- + H_2O \longrightarrow SO_4^{2-} + OH + H^+ \qquad \text{(very slow but appreciable at high conc. of } SO_4^-\text{)} \qquad (7)$$

$$2\,OH \longrightarrow H_2O + \tfrac{1}{2}\,O_2 \qquad \text{fast} \qquad (8)$$

$$CO_2^- + O_2 \longrightarrow O_2^- + CO_2 \qquad \text{slow} \qquad (9)$$

$$O_2^- + H^+ \longrightarrow HO_2 \longrightarrow HO_2^- \xrightarrow{e} H_2O_2$$

$$CO_2^- + SO_4^- \longrightarrow SO_4^{2-} + CO_2 \qquad \text{slow} \qquad (10)$$

The period of induction is the time required for the thermal activation of the $S_2O_8^{2-}$ ion so as to break into $SO_4^-$ radicals which produce $CO_2^-$ radicals responsible for the reduction of mercuric chloride.

The decrease in the period of induction in presence of 0.1 *M* sodium acetate is due to the reduction in the concentration of $H^+$ ions of the acid which exert an inhibiting influence on the reduction of mercuric chloride, possibly due to their catalysing influence on step (7) :

$$SO_4^- + H^+ \longrightarrow HSO_4 \qquad .. \qquad .. \qquad (11)$$

$$HSO_4 + H_2O \longrightarrow HSO_4^- + OH + H^+ \qquad .. \qquad .. \qquad (12)$$

with the result that the velocity of production of $CO_2^-$ radical by $SO_4^-$ (step 2) is suppressed. When the concentration of the acetate is 1.0 *M*, *i.e.*, it is in large excess compared to that of oxalic acid, it may also exert a kinetic salt effect causing decrease in the velocity of reduction (Fig. 2).

According to the above mechanism, the reduction of mercuric chloride (or the precipitation of mercurous chloride) is governed by step (4). By employing the usual steady state approximations

for the various radicals, the velocity of formation of mercurous chloride may be expressed by the equation :

$$\frac{d[Hg_2Cl_2]}{dt} = k \frac{C_{S_2O_8^{2-}} \cdot C_{C_2O_4^{2-}} \cdot C_{Hg^{2+}}}{C_{O_2}\left[1 + k' \frac{C_{S_2O_8^{2-}}}{C_{O_2}}\right]} \quad .. \quad (13)$$

where $k$ and $k'$ are constants.

Equation (13) demands that the velocity of reduction of mercuric chloride should increase by increasing the concentration of oxalic acid or mercuric chloride. Since step (7) is very slow, the concentration of dissolved oxygen may be assumed to be proportional to the volume of the reaction mixture, which is kept constant for each observation. It has been observed that oxygen exerts a very strong inhibiting influence on the reduction. Hence, on increasing the concentration of the persulphate within low values, when the ratio $C_{S_2O_8^{2-}}/C_{O_2}$ is small compared to unity, the velocity of reduction of mercuric chloride should increase, but at higher concentrations of it, when the ratio increases appreciably, the velocity of reduction should decrease. These observations are supported by data in Tables I and II.

The zero-order, exhibited by the reaction in the early stage, is due to steps (4), (5) and (6). The concentration of $CO_2^-$ is maintained constant by steps (4) and (5), and as soon as it is formed it reacts with $Hg^{2+}$ ion irrespective of its ($Hg^{2+}$) concentration, and hence, exhibits zero-order. The auto-catalysis after the period of normal velocity is due to the increase in the concentration of $SO_4^-$ radical and consequently in the rate of production of $CO_2^-$ radical by step (2), resulting in the increased velocity of reduction of mercuric chloride by step (4), which is faster than step (3). The increase in velocity continues up to a limiting value when the chain-breaking processes (7) to (10) develop and cause inhibition in the reaction. The reversibility in the reaction (*i.e.* the decrease in the amount of precipitated mercurous chloride) in the last stages is due to the action of molecular oxygen produced in step (8) on mercurous ion, as explained below :

$$Hg^+ + O_2 \longrightarrow Hg^{2+} + O_2^- \quad (14)$$

The accelerating influence of nitrogen is due to the removal of some of the dissolved oxygen from the reaction mixture and decreases its inhibiting influence. The $H^+$ ions destroy $SO_4^-$ radical which produces the $CO_2^-$ radical. Sodium acetate removes $H^+$ ions and stabilizes $SO_4^-$ radical with the result that the chains are elongated and reduction of mercuric chloride reaches to almost completion (Fig. 2). When the concentration of the acetate is in large excess compared to that of the acid, e.g. 1.0 *M*, a fraction of it reacts with $H^+$ ions and the rest exerts kinetic salt effect on the velocity of reduction of mercuric chloride (Fig. 2).

The authors express their sincere thanks to the Uttar Pradesh Scientific Research Committee, Allahabad, for a contingency grant. One of the authors (L.K.S.) is grateful to the Ministry of Education, Government of India, for the award of a scholarship. Their thanks are due to Dr. A. K. Bhattacharya, D.Sc., F.R.I.C., Professor and Head of the Chemistry Department, Agra College, for his keen interest in these investigations.

CHEMICAL LABORATORIES,
AGRA COLLEGE, AGRA.

*Received January 20, 1960.*

[Jour. Indian Chem. Soc., Vol. 37, No. 7, 1960]

# THE EFFECT OF TEMPERATURE AND VISCOSITY ON THE FLUORESCENCE OF SOLUTIONS OF SOME ORGANIC COMPOUNDS, USING UV EXCITATION

BY J. SAHU

The effect of temperature and viscosity on the fluorescence of solutions of some organic compounds, using UV excitation in low viscosity (petroleum ether and ethanol) and high viscosity (medicinal paraffin and glycerol), in the temperature range varying from -70° to 70° has been investigated. Terphenyl and carbazole have unit yields in all the solvents over the temperature range studied. Acenaphthene, 2:6-dimethylnaphthalene, naphthalene, stilbene and phenanthrene show flattish yield-temperature curves. The yields of ethyl stilbene-4:4'-dicarboxylate and stilbene-4:4'-*bis*-carbonimino-ethyl ether are markedly temperature-dependent, reach unity at low temperatures and have a large viscosity effect. The $F_0$ values of 1- and 2-naphthols in non-ionised and ionised forms are also temperature-dependent. The $F_0$ value in general increases with the increase of viscosity. The results are interpreted by an equation:

$$(1/F - 1) = k\,e^{-E/RT} + K.$$

In previous publications (Bowen and Sahu, *J. Phys. Chem.*, 1959, **63**, 4; *J. Chem. Soc.*, 1958, 3716) the effect of temperature and viscosity on the fluorescence of solutions of anthracene and its derivatives, and acridine and acridone, using excitation 3650 Å line of mercury, was studied. The present work deals with the results of a similar study on solutions of some other organic compounds.

## EXPERIMENTAL

The experimental method adopted was that of Bowen and Sahu (*loc. cit.*) with the following changes:

(*a*) The 3135 Å line of mercury (with nearly 10% of 3340 Å line) was secured as exciting light by removing the glass envelope of the mercury lamp and filtering the radiation through a strong solution of nickel and cobalt sulphates containing some copper sulphate.

(*b*) The glass prism of the spectrometer and the glass tube for holding the fluorescent solutions, fitted in the glass Quickfit flask, were all replaced by the silica ones.

(*c*) Solutions used were dilute enough to afford only partial light absorption.

(*d*) The spectrometer was adjusted to right angles to the exciting light to pick up the maximum fluorescence emission. This was tested for the satisfactory work by measuring the fluorescence of anthracene solutions in petroleum ether (b.p. 80-100°) (using a concentration providing maximum collectable fluorescence) at different temperatures.

As it was not possible to calibrate the apparatus directly after making the above changes, a terphenyl solution in petroleum ether ($c = 10^{-4}\,M/l$), its $F_0$ value being known to be unity, was chosen to act as the standard on account of its fluorescence band lying in the region in which those of the other compounds of study also fell. The $F_0$ values of the compounds were found by comparing the area under the experimentally found fluorescence band of the standard with those of the others on the assumption that the percentage correction for the sensitivity of the apparatus and that for the overlap effect would be the same for all the compounds having fluorescence bands in the same regions. However, the $F_0$ value of phenanthrene on comparison with that of anthracene ($F_0 = 0.332$), obtained by using solutions of known absolute yield (Weber and Teale, *Trans. Faraday Soc.*, 1957, **53**, 646) and terphenyl ($F_0 = 1.0$), all in petroleum ether (80-100°), was found approximately to be the same (0.155 with anthracene standard and 0.159 with terphenyl standard). The results after correction for refractive index are recorded in Table I and the effect of temperature and viscosity on the fluorescence of organic compounds in solutions is shown in Fig. 1.

## TABLE I

*Fluorescence of organic substances in solutions.*

| Compounds. | Solvents. | Region of fluorescence band. | $F_o$ at 20°. |
|---|---|---|---|
| 1. Phenanthrene | P | | 0.155 |
| | E | 4200-3400 Å | 0.210 |
| | M | | 0.188 |
| 2. Naphthalene | P | 3700-3000 | 0.393 |
| 3. 2:6-Dimethylnaphthalene | P | 3800-2900 | 0.390 |
| 4. Acenaphthene | P | 3900-3200 | 0.660 |
| 5. Stilbene | P | 3800-2800 | 0.267 |
| | M | | 0.267 |
| 6. Ethyl stilbene-4:4′-dicarboxylate | E | 4500-3500 | 0.360 |
| | G | | 0.500 |
| 7. Stilbene-4:4′-*bis*-carboniminoethyl ether | E | 4500-3500 Å | 0.425 |
| | G | | 0.610 |
| 8. Carbazole | P | 4200-2900 | 0.950 |
| | M | | 1.000 |
| 9. *p*-Terphenyl | P | 4100-2950 | 1.000 |
| 10. 1-Naphthol (*a*) Neutral EtOH (mol. form) | | 4700-3300 (max. at 3600 Å) | 0.635 |
| (*b*) Alkaline EtOH (ionic form) | | 5700-3800 (max. at 4700 Å) | 0.590 |
| 11. 2-Naphthol (*a*) Neutral EtOH (mol. form) | | 4500-2900 (max. at 3550 Å) | 0.590 |
| (*b*) Alkaline EtOH (ionic form) | | 5900-3700 (max. at 4225 Å) | 0.465 |

*N.B.*—P, M, G and E refer respectively to petroleum ether (80-100°), medicinal paraffin, glycerol and ethanol.

## DISCUSSION

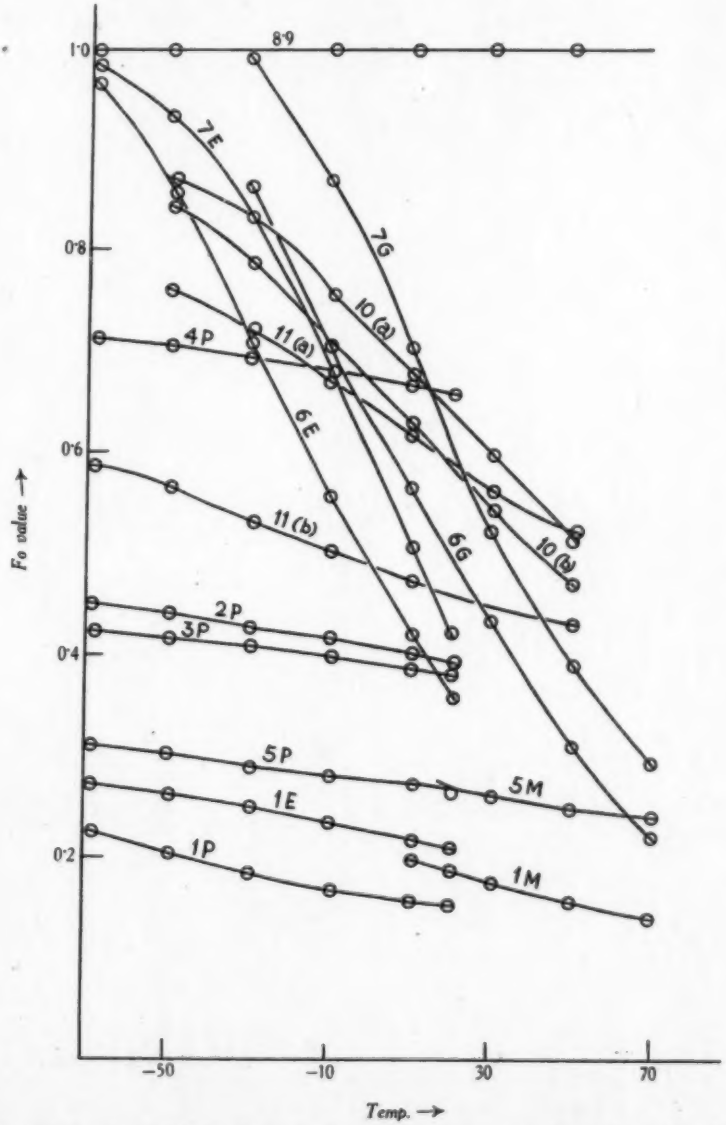
The results are interpreted making assumption of the following simple mechanism :

| Processes. | | Relative rates. |
|---|---|---|
| $A + h\nu \rightarrow {}^1A^*$ | .. (1) | 1 |
| ${}^1A^* \longrightarrow A + h\nu'$ | .. (2) | $k_f\,[{}^1A^*]$ |
| ${}^1A^* \longrightarrow {}^3A$ | .. (3) | $k_1\,[e^{-E/RT}]\,[{}^1A^*]$ |
| ${}^1A^* \longrightarrow A$ or ${}^3A$ | .. (4) | $k_2\,[{}^1A^*]$ |

Processes (1) and (2) only are in operation for carbazole and terphenyl which have the unit yields, so that $(1/F-1)=0$. For acenaphthene, 2:6-dimethylnaphthalene, naphthalene, stilbene and phenanthrene, which show flattish yield-temperature curves, all the above four processes are in operation; for ethyl stilbene-4:4′-dicarboxylate and stilbene-4:4′-*bis*-carboniminoethyl ether and 1- and 2-naphthols, in non-ionic and ionic forms, the first three processes are in operation. The process (3) is suggested on the basis of the simple hypothesis that out of the two processes of energy degradation, one temperature-dependent with a large viscosity effect and the other temperature-independent, the former may be due to the return of singlet excited molecules to the triplet undergoing some bent or twisted configuration (assuming some energy of activation) whose amplitude of bending or twisting is restricted in highly viscous solvents. Equation (4) is proposed to explain the temperature-independent process. In this process whether the singlet excited molecules return to the normal state through a non-radiational process or to the triplet state needing no energy of activation, is very difficult to suggest. If the return to the normal state through a non-radiational process is the only possible one, then the compounds would not be expected to phosphoresce efficiently at low temperatures. It has been suggested by Livingston ("Photochemistry of Liquid and Solid States", John Wiley & Sons, Inc., 1960, p. 77, that in the photo-oxidation of anthracene in bromobenzene, the singlet excited molecules may partly return directly to the normal

state through a non-radiational process. If it is so, then the compounds showing flattish yield-temperature curves might have their triplet state curves crossing the singlet excited curves above the zero-vibrational level of the latter, and their singlet curves closely approximating to the ground level potential energy curves near the minimum so that the singlet excited molecules may pass over to the triplet level with some small energy of activation and also to the normal state directly

FIG. 1




The numbers and symbols in Fig. 1 correspond respectively to the compounds and solvents shown in Table I.

with little activation energy, whereby the fluorescence yields do not reach unity at low temperatures; the reverse may also be true.

The compounds having unit yields over the whole temperature range then return from the singlet excited state through a radiational process only to the normal state, as might occur if the triplet state curves crossed the singlet excited state curves much above the zero-vibrational level of the latter and the singlet excited state curves did not closely touch the normal potential energy curves.

The compounds showing steep temperature-dependent yields and those reaching unity at low temperatures might have then the triplet state curves crossing the singlet excited above the zero-vibrational level of the latter, but the singlet excited not touching the normal.

Change of viscosity definitely produces a considerable effect on the fluorescence yields, but it has not been possible to interpret the effect clearly; however, the tentative explanation advanced by Bowen and Sahu (*loc. cit.*), may also be applicable in these cases.

From the equation :

$$(1/F - 1) = k\, e^{-E/RT} + K$$

(which can be deduced from the above mechanism) the values of $E$ and $k$ for some compounds have been calculated (Table II).

TABLE II

| * Compounds. | ** Solvents. | $E$. | $k$. |
|---|---|---|---|
| (6) | E | 4300 cal./mol. | 2760 |
| | G | 4700 | 3067 |
| (7) | E | 5500 | 16000 |
| | G | 6000 | 16800 |
| (10) | | | |
| (*a*) Mol. form | E | 3000 | 95 |
| (*b*) Ionic form | E | 2850 | 92 |
| (11) | | | |
| (*a*) Mol. form | E | 1850 | 16.4 |
| (*b*) Ionic form | E | 850 | 5.0 |

* The number of compounds corresponds to those shown in Table I.
** Symbols have the same significance as in Table I.

The $E$-values of the ionised and non-ionised forms of both the 1- and 2-naphthols differ from each other. This difference is much more marked in 2-naphthol than in 1-naphthol. This may be ascribed to ionisation effecting a considerable change in the electronic structure of the molecules (Bowen and Wokes, "Fluorescence of Solutions", 1953, p. 10).

*Oxygen Quenching.*—Quenching of fluorescence of solutions of these organic compounds by oxygen has also been studied. Phenanthrene in petroleum ether has a marked oxygen-quenching effect whereas in ethanol its fluorescence is not quenched. Naphthalene, 2:6-dimethylnaphthalene, acenaphthene and carbazole, all in petroleum ether, show oxygen quenching, whereas stilbene and its derivatives do not show any quenching by oxygen.

The author's sincere thanks are due to Dr. E. J. Bowen of Oxford University for his helpful and valuable suggestions.

PHYSICAL CHEMISTRY LABORATORY,
L. S. COLLEGE, MUZAFFARPUR, BIHAR UNIVERSITY.

*Received February* 19, 1960.

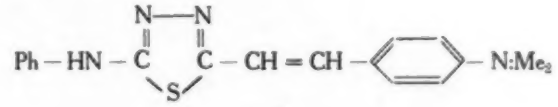
[Jour. Indian Chem. Soc., Vol. 37, No. 7, 1960]

# *p*-DIALKYLAMINOSTYRYL DYES DERIVED FROM 5-ARYLAMINOTHIADIAZOLES

BY P. B. TRIPATHY AND M. K. ROUT

By condensation of the following pairs: (1) 5-phenylamino-2-methylthisdiazole and *p*-dimethylaminobenzaldehyde, (2) 5-phenylamino-2-methylthiadiazole and *p*-dimethylaminobenzaldehyde methiodide, (3) 5-phenylamino-2:3-dimethylthiadiazolium iodide and *p*-dimethylaminobenzaldehyde, three compounds (one colorless, one yellow and the third, red) have been obtained and their colours explained in terms of resonance theory. Six 5-arylamino-2:3-dimethyl-1:3:4-thiadiazolium iodides have also been prepared and condensed with *p*-dimethylaminobenzaldehyde and *p*-diethylaminobenzaldehyde to yield the corresponding *p*-dialkylaminostyryl dyes. Their absorption spectra have been measured and their deviations calculated and compared with the deviations obtained in case of *p*-dialkylaminostyryl dyes derived from quinoline, benzothiazole and thiazoles. Since deviations are a measure of basicity, the greater deviation of dyes derived from thiadiazoles indicates that it is more basic than benzothiazole or quinoline. The sensitisation spectra of dialkylaminostyryl dyes have also been measured.

2-*p*-Dimethylaminostyryl-5-phenylamino-1:3:4-thiadiazole(I), formed by the condensation of 5-phenylamino-2-methyl-1:3:4-thiadiazole with *p*-dimethylaminobenzaldehyde, gives rise to two mono-methiodides, one a red compound and the other, almost colorless (separated by fractional crystallisation). The red compound is identical with the product formed by condensation of 5-phenylamino-2:3-dimethyl-1:3:4-thiadiazolium iodide with *p*-dimethylaminobenzaldehyde, and the colorless compound could also be similarly obtained by condensing the methiodide of *p*-dimethylaminobenzaldehyde with 5-phenylamino-2-methyl-1:3:4-thiadiazole. The existence of resonance and the long conjugated chain contribute to the deep colour in the red compound. The yellow colour of the base (I) is due to the fact that degeneracy of the system, neutral→charged structure, is very low.

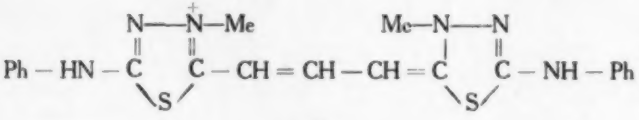


(I)

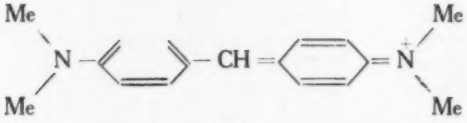
In the present investigation, several 5-arylamino-2-methyl-1:3:4-thiadiazoles have been prepared. Their corresponding thiadiazolium iodides have been condensed with *p*-dimethylamino- and *p*-diethylamino-benzaldehydes to give rise to the corresponding *p*-dialkylaminostyryl dyes. The absorption spectra of the dyes have been measured in the visible spectrophotometer (Unicam S.P. 600).

In order to estimate the basicity of the thiadiazole nucleus, relative to benzothiazole and quinoline etc., the deviation observed in *p*-dialkylaminostyryl dye (I) has been compared with that shown by the corresponding dyes derived from benzothiazole, quinoline and thiazole. It is known that the greater the deviation shown by a styryl dye, the greater is the basicity of the nitrogen heterocyclic ring involved. The deviation has been calculated by regarding the dye (I)

as the structural cross between the symmetrical dye (II) and the acidified form of Michler's hydrol (III). Calculating in this manner, the deviations of the dyes derived from thiadiazole, quinoline and benzothiazole compounds have been found to be 85, 80, 45 mμ respectively, thus showing that 5-phenylaminothiadiazole nucleus is more basic than either quinoline or benzothiazole.

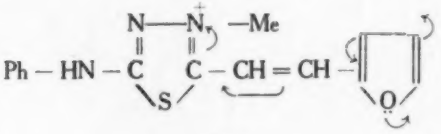


(II)

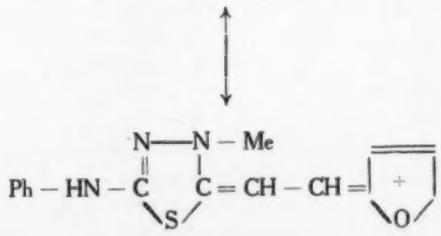


(III)

In order to examine the absorption spectra of styryl-cyanine system in which the resonance interaction of *N*-dimethylamino group is absent, 5-phenylamino-2:3-dimethylthiadiazolium odide has been condensed with furfuraldehyde and thiophene-2-aldehyde. The colour of this system may be attributed to resonance between the structures (IVa) and (IV b). These compounds absorb at much shorter wave-lengths, thus indicating a sufficiently high energetic asymmetry between the two extreme structures.

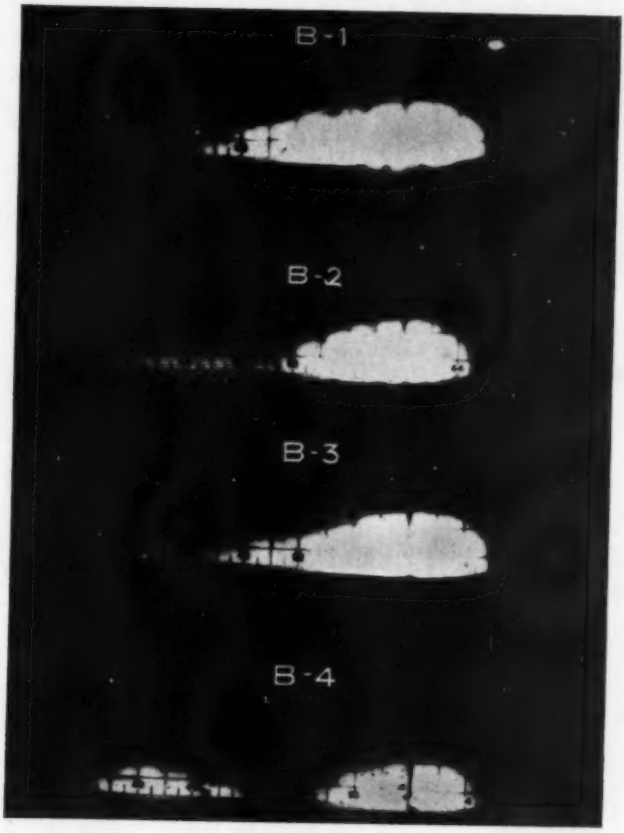


(IV a)



(IV b)

The sensitisation spectra of some of the compounds have also been measured by the method of Doja *et al.* (this *Journal*, 1941, **18,** 281) with slight modifications.




The light source was a 100 watt tungsten lamp instead of a 100 C.P. (point-o-lite) lamp. An wedge was placed in front of the slit to serve the purpose of rotating logarithmic sector used by Doja and co-workers. An internal scale was used to read the wave-length.

## EXPERIMENTAL

*5-p-Tolylamino-2:3-dimethyl-1:3:4-thiadiazolium Iodide.*—The base, 5-*p*-tolylamino-2-methyl-1:3:4-thiadiazole, was prepared by the action of acetyl chloride (6-7 c.c.) on ice-cooled *p*-tolylthiosemicarbazide (3 g.), the latter being obtained by reacting an ice-cooled 50% solution of hydrazine hydrate with an ice-cooled ethanolic solution of *p*-tolyl *iso*thiocyanate. On completion of the reaction the excess of acetyl chloride was removed and the syrupy mass was treated with ammonia to yield the base. It was crystallised from ethanol, m.p. 194°, yield 78%.

The corresponding iodide was prepared by heating the above base (1 *M*) with methyl iodide (1.2 *M*) in a sealed tube for 48 hours at 100°. The solid, isolated from the reaction mixture, was

washed with ether and crystallised from ethanol, m.p. 182°, yield 90%. (Found : I, 36.5. $C_{11}H_{13}N_3IS$ requires I, 36.7%).

The properties and analytical data etc. of other thiadiazoles and their corresponding methiodides are shown in Table I.

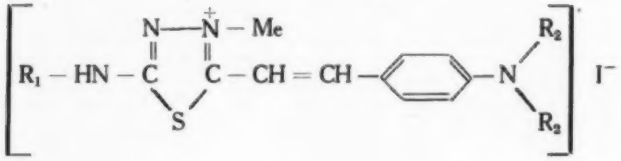
TABLE I

| Nature of R. | M. P. of the base. | Methiodides. Yield. | M.P. | % Iodine. Found. | Calc. |
|---|---|---|---|---|---|
| *o*-Tolyl | 203° | 73% | 198° | 36.60 | 36.70 |
| Phenyl | 191° | 80 | 163° | 36.20 | 38.25 |
| *p*-Ethoxyphenyl | 178° | 72 | 203° | 32.78 | 32.70 |
| *p*-Methoxyphenyl | 167° | 82 | 186° | 34.90 | 34.98 |
| *p*-Bromophenyl | 234° | 80 | 162° | 30.71 | 30.82 |

5-p-*Tolylamino*-2-p-*dimethylaminostyryl*-3-*methylthiadiazolium Iodide*.—To a mixture of 5-*p*-dimethylamino-2:3-dimethyl-1:3:4-thiadiazolium iodide (0.32 g.) and *p*-dimethylaminobenzaldehyde (0.15 g.), dissolved in absolute ethanol (10 c.c.), piperidine (2 drops) was added and the mixture refluxed for 4 hours. It was chilled ; the fine needle-shaped crystals separating were washed with ether and finally crystallised from ethanol, m.p 182°, yield 58%. (Found: C, 49.9; H, 4.88. $C_{20}H_{23}N_4IS$ requires C, 50.1; H, 4.8%). It shows absorption maximum at 480 mμ.

The properties and analytical data of other compounds of this series are recorded in Table II.

TABLE II



| No. | $R_1$. | $R_2$. | $\lambda_{max.}$ | M.P. | Yield. | % Carbon. Found. | Calc. | % Hydrogen. Found. | Calc. |
|---|---|---|---|---|---|---|---|---|---|
| 1. | *p*-Tolyl | Et | 491 mμ | 228° | 47% | 52.10 | 52.07 | 5.35 | 5.52 |
| 2. | *o*-Tolyl | Me | 480 | 118° | 38 | 49.78 | 50.10 | 4.90 | 5.01 |
| 3. | ,, | Et | 490 | 130° | 33 | 52.00 | 52.07 | 5.38 | 5.52 |
| 4. | Phenyl | Me | .. | 222° | 47 | 49.20 | 49.03 | 4.58 | 4.50 |
| 5. | ,, | Et | .. | 207° | 35 | 51.30 | 51.10 | 4.98 | 5.20 |
| 6. | *p*-Ethoxyphenyl | Me | .. | 240° | 30 | 49.52 | 49.60 | 4.70 | 4.90 |
| 7. | ,, | Et | .. | 216° | 38 | 51.62 | 51.70 | 5.31 | 5.40 |
| 8. | *p*-Methoxyphenyl | Me | .. | 240° | 36 | 48.81 | 48.90 | 4.50 | 4.64 |
| 9. | ,, | Et | .. | 216° | 43 | .. | .. | .. | .. |
| 10. | *p*-Bromophenyl | Me | .. | 262° | 42 | 41.94 | 41.90 | 3.58 | 3.70 |
| 11. | ,, | Et | .. | 218° | 40 | .. | .. | .. | .. |

*6-Methyl-2-p-dimethylaminostyryl-1-ethylquinolinium Iodide.*—A mixture of 2:6-dimethylquinoline ethiodide (0.31 g.) and *p*-dimethylaminobenzaldehyde (0.14 g.), dissolved in ethanol (10 c.c.), was refluxed for 2 hours after addition of piperidine (2 drops). On cooling, the solid separating was collected and crystallised from ethanol as deep red needles, m.p. 254°, yield 62%.

Similarly were prepared the following: 6-Methyl-2-*p*-diethylaminostyryl-1-ethylquinolinium iodide, 4-*p*-bromophenyl-2-*p*-dimethylaminostyryl-3-methylthiazolium iodide and 4-*p*-bromophenyl-2-*p*-diethylaminostyryl-3-methylthiazolium iodide.

*2-p-Dimethylaminostyryl-5-phenylamino-1:3:4-thiadiazole.*—A mixture of 5-phenylamino-2-methyl-1:3:4-thiadiazole (3 g.) and *p*-dimethylaminobenzaldehyde (1.14 g.), dissolved in ethanol (20 c.c.), and piperidine (2 drops) was refluxed in a steam-bath for 6 hours. Excess of alcohol was removed and on cooling, a solid separated out which was collected and crystallised from ethanol as colorless cubes, m.p. 172°, yield 70%. (Found: S, 9.85. $C_{18}H_{18}N_4S$ requires S, 9.9%).

The methiodide of the above compound was prepared by heating the thiadiazole (3.2 g.) and MeI (1.8 g.) in a sealed tube for 24 hours. The product obtained after washing with ether was deep red in colour. It was crystallised. The first fraction which crystallised out was red in colour and had m.p. 220° and found to be identical with compound No. 4 of Table II.

The second fraction which crystallised out was almost colorless and had m.p. 191°. (Found: C, 49.3; H, 4.6. $C_{19}H_{21}N_4IS$ requires C, 49.03; H, 4.5%).

*5-Phenylamino-3-methyl-2-(2-thenylvinyl)-1:3:4-thiadiazolium Iodide.*—A mixture of 5-phenylamino-2:3-dimethyl-1:3:4-thiadiazolium iodide (3 g.) and thiophene-2-aldehyde (1 g.), dissolved in absolute ethanol (10 c.c.), and piperidine (2 drops) was refluxed for 2 hours. It was cooled and the excess of alcohol removed under reduced pressure. The resulting gum was washed several times with ether. On crystallisation from ethanol yellow plates were obtained, m.p. 244°, yield 40%. It shows absorption maximum at 415 mμ.

*5-Phenylamino-3-methyl-2-(2-furylvinyl)-1:3:4-thiadiazolium Iodide.*—5-Phenylamino-2: 3-dimethyl-1:3:4-thiadiazolium iodide (3 g.) and furane-2-aldehyde (12 g.) were used for the preparation of this compound. It was isolated in the same manner as above, when the product was obtained as brown crystals, m.p. 238° (decomp.), yield 52%. It shows absorption maximum at 422 mμ.

*Sensitisation.*—The sensitisation spectra of four compounds, namely, compounds No. 4, 5, 10 and 11 of Table II are given. Refer to photographs, B-1 (Comp. No. 4), B-2 (Comp. No. 5). B-3 (Comp. No. 10), B-4 (Comp. No. 11) and the photograph without any mark is that of the unsensitised plate.

The authors are thankful to the Board of Scientific and Industrial Research for research grants to carry out this investigation and to Mr. M. Q. Doja, B.A. (Cantab), Principal, Science College, Patna, for his kind help in carrying out the experiments on measurments of sensitisation spectra.

MAYURBHANJ CHEMICAL LABORATORY,
RAVENSHAW COLLEGE, CATTACK.

*Received December 4, 1959.*

[Jour. Indian Chem. Soc., Vol. 37, No. 7, 1960]

# ISOLATION OF SCOPOLETIN, SKIMMIN AND UMBELLIFERONE FROM THE TRUNK-BARK OF *SKIMMIA LAUREOLA* HOOK

BY S. R. BHATTACHARJEE AND D. K. MULLICK

Scopoletin, skimmin and umbelliferone have been isolated from the trunk-bark of *Skimmia laureola* Hook.

The leaves and the bark of *S. laureola* had been reported to contain a number of coumarin derivatives (Chatterjee and Bhattacharjee, this *Journal*, 1953, **30**, 33; *Curr. Sci.*, 1947, **16**, 222), but the occurrence of scopoletin in this plant had not been reported. Probably it could not be isolated because of its poor solubility in ether, which was employed by earlier workers. Scopoletin (0.035%), skimmin (0.50%) and umbelliferone (0.04%) have been isolated by the present authors in pure forms from the trunk-bark of *S. laureola*. Extraction with chloroform furnished a higher yield of scopoletin (0.025-0.035%) than that obtained by extraction with ether (0.005%).

The defatted trunk-bark after ether and chloroform extraction was percolated with ethanol from which skimmin, m.p. 204-208° (decomp.), had been obtained. On hydrolysis it yielded umbelliferone and glucose. The latter was identified as its osazone, m.p. 202°.

From the chloroform extract of the trunk-bark of the plant, another coumarin crystallised in star-shaped needles, m.p. 186-88.° It was obtained in poor yield (0.0005%) and gave identical colour reactions as scopoletin. Further work on this compound could not be done owing to paucity of the material.

The identity of coumarin, $C_{10}H_8O_4$, m.p. 202°, obtained from *S. laureola* Hook, with scopoletin has been established from mixed m.p., chemical analysis and spectral measurements of the compound and its derivatives. On methylation with diazomethane, the compound forms a dimethoxycoumarin, $C_{11}H_{10}O_4$, m.p. 144°. The latter has been shown to be identical with aesculetin dimethyl ether.

## EXPERIMENTAL

Air-dried and powdered trunk-bark (1.0 kg.) was defatted with petroleum ether (b.p. 40-60°) for 24 hours and then soxhletted with ether (2 litres) for 60 hours. The ether extract (P) was kept aside. After ether extraction, the marc was extracted with chloroform for 60 hours. The chloroform extract was freed of the solvent when a pasty resinous mass (Q) separated.

### *Isolation of Skimmin*

The defatted trunk-bark (100 g.), previously extracted with ether and chloroform, was percolated in cold with aqueous ethanol (60%). The brown extract (500 c.c.) was concentrated to 150 c.c. under vacuum at 50-60°. The insoluble resinous matter separated out and the supernatant solution was shaken with ether. The aqueous solution was removed and treated with a saturated lead acetate solution in excess. The lead precipitate was filtered off. The filtrate was treated with $H_2S$. The precipitated lead sulphide was removed. The light brown solution was then

concentrated under vacuum to a syrupy consistency (5 c.c.). No crystalline solid separated and the solution was subsequently evaporated to dryness in vacuum at room temperature. A sticky mass was obtained. It was taken up in methanol (50 c.c.) and treated with norite. The pale yellow solution was evaporated to dryness under vacuum when a light brown hygroscopic crystalline solid was obtained (0.5 g.). The compound decomposed above 210° with previous shrinking at 206°. (Found in a dry sample : C, 54.98 ; H, 4.82. Calc. for $C_{15}H_{16}O_8$ : C, 55.55; H, 4.94%). The glucoside was hydrolysed with 5% $H_2SO_4$ for 6 hours on a water-bath. The solution was then cooled and shaken with ether. Umbelliferone was obtained from the ether extract which on crystallisation from ethyl acetate yielded colorless needles, m.p. 222-23°. It showed no depression in m.p. when admixed with an authentic sample of umbelliferone. The aqueous solution after removal of umbelliferone was neutralised with sodium carbonate and decolorised with norite, and treated with phenylhydrazine acetate. In about 10-15 mins. at the temperature of water-bath, yellow precipitate (sheaves of corn under a microscope) appeared. It was crystallised from dilute ethanol in yellow needles, m.p. 202-204°. Mixed m.p. with glucosazone remained undepressed.

*Isolation of Umbelliferone and Scopoletin from Ether Extract (P)*

The deep wine-red ether extract (P) was concentrated to half its bulk and shaken with 2*N*-HCl (3 × 200 c.c.). The brown ether solution (A) was kept aside. The wine-red aqueous acid layer was cooled and made alkaline with sodium bicarbonate and shaken with chloroform. The chloroform layer was separated from the alkaline solution (B). It was washed with water. The washings were added to (B) which was made feebly acidic (*p*H 2-3) and shaken with ether (4×250 c.c.). The ether extract was washed with a small quantity of saturated ammonium sulphate solution. It was dried over anhydrous sodium sulphate and the solvent was completely removed. The white solid was crystallised from ethyl acetate when scopoletin (0.05 g.) was obtained in colorless needles, m.p. 202°. It showed no depression in melting point with an authentic sample of scopoletin when admixed. [Found in a dry sample : C, 62.48; H, 4.13; OMe, 16.2; M.W., 196 (by Rast). Calc. for $C_{10}H_8O_4$ : C, 62.5; H, 4.17; OMe, 16.14%; M.W., 192]. The compound showed the following peak absorptions : $\lambda_{max}$ at 230mμ (log ε 4.18), 255mμ (log ε 3.79) and 347mμ (log ε 4.09); $\lambda_{max}$ at 2.97 μ (— OH), 5.85 μ (conjugated lactone), 6.10 μ (unsaturation), 6.2 μ (phenyl nucleus), characteristic of scopoletin.

*Methylation of scopoletin* was performed by treating a methanolic solution of the substance with diazomethane in ether. The monomethylscopoletin was crystallised from methanol in colorless needles, m.p. 118°. (Found in a dry sample : C, 64.29; H, 5.48; OMe, 30.56. Calc. for $C_{11}H_{10}O_4$ : C, 64.07; H, 5.34; OMe, 30.09%).

*Isolation of Umbelliferone from 'A' (vide supra)*

The brown ether solution was washed with water and then shaken carefully with 2% sodium bicarbonate solution (500 c.c.). The alkaline layer with a violet fluorescence was acidified (*p*H 2-3) when umbelliferone separated. It was taken up in ether and the solution was washed with water and dried over anhydrous sodium sulphate. The solvent was then removed to a small bulk and kept in a refrigerator overnight, when crude umbelliferone (0.5 g.), m.p. 220-27°, was obtained. It was crystallised from ethyl acetate in colorless needles (0.4 g.), m.p. 222-24°. (Found in a dry sample : C, 66.71; H, 3.72. Calc. for $C_9H_6O_3$ : C, 66.66; H, 3.68%). The compound did not depress the m.p. of an authentic sample of umbelliferone when admixed. Its methyl ether, $C_9H_5O_2.OCH_3$, melted at 118-19°. (Found in a dry sample : C, 68.20; H, 4.61; OMe, 17.7. Calc. for $C_{10}H_8O_3$: C, 68.18; H, 4.54; OMe, 17.61%).

*Isolation of Scopoletin from Fraction (Q) (vide supra)*

The fraction (Q) was refluxed with dry benzene (500 c.c.) for 2 hours when most of the resin dissolved. The benzene solution was cooled and decanted. The clear benzene solution was carefully shaken with 2*N*-HCl (3×200 c.c.). The yellow aqueous acid layer was separated and treated with sodium bicarbonate till the *p*H of the solution was 2 to 3. It was then vigorously shaken with a litre of ether (4×250 c.c.). The ether solution was washed with a saturated ammonium sulphate solution, dried over anhydrous sodium sulphate and concentrated on a water-bath to about 20 c.c., when scopoletin (0.35 g.), m.p. 185-92°, separated as a granular solid. On repeated crystallisations from ethyl acetate, it yielded colorless needles (0.30 g.), m.p. 202°. From the mother-liquor coumarin, m.p. 186-88° (0.005 g.), was obtained.

The authors express their sincere thanks to Principal A. C. Roy, Bengal Engineering College, and Professor B. Chatterjee, Head of the Department of Chemistry and Metallurgy, Bengal Engineering College, for providing facilities for research work and to Dr. (Mrs.) A. Chatterjee, Reader, University College of Science, Calcutta, for her interest in this work.

Department of Chemistry,
Bengal Engineering College,
Sibpur, Howrah.

*Received December 12, 1959.*

[Jour. Indian Chem. Soc., Vol. 37, No. 7, 1960]

# ORGANIC PESTICIDES. PART II. PREPARATION OF SOME *N*-SUBSTITUTED FLUOROBENZAMIDES

By K. C. Joshi and S. Giri

Several *N*-substituted fluorobenzamides have been prepared, preliminary to evaluation of their pesticidal activity.

Organic fluorine compounds have recently assumed industrial importance in the general field of pest control. Amongst the large number of compounds tested so far, substituted fluoroacetamides of the type, $FCH_2CONHR$, have been extensively investigated by Saunders ("Phosphorus and Fluorine", Cambridge University Press) and Bergman (*J. Sci. Food Agr.*, 1957, **8**, 400). These workers have reported the use of such compounds as contact insecticides, potential larvicides and rodenticides. The magnitude of toxicity of $FCH_2CONHR$ suggests that all such compounds are hydrolysed in the animal body to fluoroacetic acid, and the effective part of the molecule is the $CH_2F$-group (Saunders, *J. Chem. Soc.*, 1949, 912 ; *loc. cit.*). These fluoroacetamides, however, also act as convulsant poisons with delayed action, and special precautions must be taken while handling these toxic compounds.

Keeping these observations in view, we have prepared *N*-substituted fluorobenzamides as potential pesticides. A large number of aromatic fluorine compounds, like, 2:4-difluorobenzoic acid and 2:4:5-trifluorobenzoic acid, have been found to be fungicidal by Finger *et al.* (Ill. State Geological Survey, Circular 199, 1955), indicating that the substitution of fluorine in the aromatic nucleus is likely to confer fungicidal activity on the unsubstituted aromatic compounds. We therefore expect that the conversion of fluorobenzoic acids into the corresponding amides will further enhance their toxicity as certain substituted benzamides, like, *N*-substituted *o*-nitrobenzamides, have already been patented as effective seed disinfectants against many fungi (Brien *et al.*, U.S.P. 2,643,965/1953). Besides, these compounds will be safer to handle than the corresponding fluoroacetamides due to the moderating influence of the aromatic nucleus.

In this communication, *N*-substituted fluorobenzamides, derived from *p*-fluorobenzoic acid and *o*-fluorobenzoic acid, have been prepared. The latter have been obtained from ethyl *p*-aminobenzoate and ethyl anthranilate respectively by the Balz-Schiemann reaction. The fluorobenzoic acids have been converted into the corresponding acid chlorides by the action of thionyl chloride, and the *N*-substituted fluorobenzamides were obtained by the action of different amines on the fluorobenzoyl chlorides in anhydrous benzene medium (Shriner, Fuson and Curtin, "The Systematic Identification of Organic Compounds", p. 227).

## Experimental

*Ethyl* p-*fluorobenzoate* was prepared by a modification of the original Balz-Schiemann method (*Ber.*, 1927 **60**, 1186). Ethyl *p*-aminobenzoate (110 g.) was dissolved in a mixture of HCl (conc., 137 c.c.) and water (198 c.c.) and diazotised as usual with a solution of sodium nitrite (50 g.) in a minimum quantity of water. A solution of sodium fluoborate [prepared by mixing acid boric (46 g.) with HCl (conc., 180 c.c.) and then adding sodium fluoride (120 g.) at intervals at 0°] was added to the diazotised solution at 0°; the resultant product was allowed to stand for one hour, filtered and dried, yield 87 g. (69%). Pyrolysis of diazonium fluoborate at 90-93° afforded crude ethyl *p*-fluorobenzoate, which was exracted with ether, and after removal of ether, was distilled as a reddish yellow liquid, b.p. 112-13°/35-40 mm, yield 61 g. (55%); Schiemann *et al.* ("Organic Syntheses" Vol. 2, p. 299, 1943) report b.p. 105-106°/25 mm.

*p-Fluorobenzoic Acid.*—Ethyl *p*-fluorobenzoate (61 g.) was hydrolysed with 28% ethanolic KOH solution under reflux and *p*-fluorobenzoic acid precipitated as a yellowish solid on neutralisation

with HCl (conc.). Reprecipitation from dilute $K_2CO_3$ solution furnished the pure acid, m.p. 184-85°, yield 27 g. (53%). Schiemann *et al.* (*loc. cit.*) report m.p. 184-86°.

*Ethyl o-Fluorobenzoate.*—Ethyl *o*-aminobenzoate (80 g.) was diazotised and converted into diazonium fluoborate, as described above. On pyrolysis at 104-107°, the latter gave crude ethyl *o*-fluorobenzoate which was isolated as a yellowish liquid, b.p. 119-21°/55-60 mm, yield 56 g. (51%). Lit. records b.p. 209° (Beil., IX-137).

*o-Fluorobenzoic Acid.*—Ethyl *o*-fluorobenzoate (56 g.) was hydrolysed and the acid isolated as described above, m.p. 121-22°, yield 25 g. (49%). Lit. m.p., 126.5°.

p-*Fluorobenzoyl chloride* was prepared by heating a mixture of *p*-fluorobenzoic acid (27 g.) and thionyl chloride (72 g.) for about 3 hours on a water-bath. After removal of excess of thionyl chloride, *p*-fluorobenzoyl chloride was distilled under reduced pressure as a yellowish liquid, b.p. 42-44°/5 mm, yield 26 g. (83.8%). Cohen (*J. Chem. Soc.*, 1911, **99**, 1063) reports b.p. 191-92°/104 mm.

*o-Fluorobenzoyl Chloride.*—A mixture of *o*-fluorobenzoic acid (25 g.) and thionyl chloride (67 g.) was refluxed as described above and *o*-fluorobenzoyl chloride isolated as a colorless liquid, b.p. 48-52°/50-60 mm, yield 23 g. (74.2%). Lit. records b.p. 204-206° (Beil., IX-136.)

N-*Substituted Fluorobenzamides.*—To a solution of the required amine (2 *M*), in dry benzene, was added dropwise and with frequent shaking, a solution of the appropriate fluorobenzoyl chloride (1 *M*) in dry benzene. The resultant mixture was refluxed for about an hour and the product left overnight. The solution was filtered, the precipitate was washed with warm benzene and this washing mixed with the original filtrate. The benzene solution was then washed with 2% $Na_2CO_3$ solution, followed by 2% HCl, and finally with water. The benzene was distilled off and the residual amide was recrystallised from aqueous ethanol. In certain cases, pyridine was added in traces to improve the yield of the amides. The following amides have been obtained

TABLE I

N-*Substituted fluorobenzamides.*

(F denotes fluorobenzamide)

| No. | Amides. | M.P. | Yield. | Mol. formula. | % Nitrogen. Found. | Calc. |
|---|---|---|---|---|---|---|
| 1. | *p*-F | *152-53° | 51% | $C_7H_6ONF$ | 9.97 | 10.07 |
| 2. | *N*-Ethyl-*p*-F | 70° | 59 | $C_9H_{10}ONF$ | 8.14 | 8.37 |
| 3. | *N*-(Butyl$^n$)-*p*-F | 56° | 68 | $C_{11}H_{14}ONF$ | 7.02 | 7.17 |
| 4. | *N*-Phenyl-*p*-F | 180° | 64 | $C_{13}H_{10}ONF$ | 6.49 | 6.51 |
| 5. | *N*-Benzyl-*p*-F | 129-30° | 66 | $C_{14}H_{12}ONF$ | 5.89 | 6.11 |
| 6. | *N*-(*m*-Bromophenyl)-*p*-F | 128° | 54 | $C_{13}H_9ONBrF$ | 4.49 | 4.76 |
| 7. | *N*-(*p*-Bromophenyl)-*p*-F | 166-67° | 60 | $C_{13}H_9ONBrF$ | 4.52 | 4.76 |
| 8. | *N*-(*o*-Bromophenyl)-*p*-F | 110-11° | 72 | $C_{13}H_9ONBrF$ | 4.51 | 4.76 |
| 9. | *N*-(*o*-Chlorophenyl)-*p*-F | 109-10° | 71 | $C_{13}H_9ONClF$ | 5.52 | 5.61 |
| 10. | *N*-(*o*-Tolyl)-*p*-F | 112° | 50 | $C_{14}H_{12}ONF$ | 6.02 | 6.11 |
| 11. | *N*-Phenylamino-*p*-F | 96-97° | 40 | $C_{13}H_{11}ON_2F$ | 11.61 | 12.17 |
| 12. | *N*-Phenyl-*o*-F | 84-85° | 67 | $C_{13}H_{10}ONF$ | 6.46 | 6.51 |
| 13. | *N*-Benzyl-*o*-F | 39-40° | 63 | $C_{14}H_{12}ONF$ | 5.91 | 6.11 |
| 14. | *N*-(*o*-Chlorophenyl)-*o*-F | 76° | 61 | $C_{13}H_9ONClF$ | 5.42 | 5.61 |
| 15. | *N*-(*p*-Chlorophenyl)-*o*-F | 126-27° | 52 | $C_{13}H_9ONClF$ | 5.53 | 5.61 |
| 16. | *N*-(*o*-Anisyl)-*o*-F | 110° | 34 | $C_{14}H_{12}O_2NF$ | 5.52 | 5.71 |

* Lit. m.p. 153°.

The authors wish to thank Dr. R. C. Mehrotra, Professor and Head of the Department of Chemistry, University of Gorakhpur, for providing all possible facilities.

DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF GORAKHPUR, GORAKHPUR.

*Received February* 12, 1960

[Jour. Indian Chem. Soc., Vol. 37, No. 7, 1960]

# BEHAVIOUR OF CHLORONITROBENZENES WITH HYDRAZINE AND HYDRAZINE DERIVATIVES. PART X. PREPARATION OF SCME NITROPHENYLHYDRAZINES AND THEIR HYDRAZONES

By H. G. Garg and S. S. Joshi

3:4-Dibromo-6-nitro-, 2:3-dibromo-4:6-dinitro- and 2-bromo-3-chloro-4:6-dinitro-phenylhydrazines have been obtained by replacing a halogen or a nitro group by a hydrazine (-NH-$NH_2$) group. The corresponding hydrazones have also been prepared.

In the previous communications (Joshi *et al.*, this *Journal*, 1951, **28,** 34; 1952, **29,** 46; 1959, **36,** 417, 505), the preparation of a number of nitrophenylhydrazines has been described. In this paper, 3:4-dibromo-6-nitro-, 2:3-dibromo-4:6-dinitro- and 2-bromo-3-chloro-4:6-dinitro-phenylhydrazines have been synthesised by the action of hydrazine hydrate on 3:4-dibromo-1:6-dinitro- (Austen, *Ber.*, 1875, **8,** 1182), 1:2:3-tribromo-4: 6-dinitro-(Joshi and Saxena, this *Journal*, 1953, **30,** 598) and 1 : 3-dichloro-2-bromo-4 : 6-dinitro-(Joshi and Saxena, *loc. cit.*) benzenes.

The structures of the hydrazine derivatives follow from the method of their synthesis. Nitrophenylhydrazines are all coloured crystalline compounds. These are quite reactive and easily combine with carbonyl compounds to form the corresponding phenylhydrazones.

## *Experimental

*3:4-Dibromo-6-nitrophenylhydrazine.*—3:4-Dibromo-1:6-dinitrobenzene, dissolved in an excess of ethanol, was treated with an equivalent quantity of hydrazine hydrate. On cooling, a coloured crystalline solid began to separate. After about 24 hours the mass was collected. It was recrystallised from an excess of ethanol as orange-red crystals (75%), m.p. 204°. (Found: C, 23.0; H, 1.4; N, 13.3; Br, 51.2. $C_6H_5O_2N_3Br_2$ requires C, 23.1; H, 1.6; N, 13.5; Br, 51.4%).

2 : 3-*Dibromo*-4:6-*dinitrophenylhydrazine* was also obtained when a solution of 1:2:3-tribromo-4:6-dinitrobenzene in ethanol was treated with an equimolecular quantity of hydrazine hydrate, and kept overnight. Dibromodinitrophenylhydrazine separating was slightly soluble in ethanol and crystallised from an excess of the solvent in greenish yellow crystals (72%), m.p. 201°. (Found: C, 20.1; H, 1.0; N, 15.3; Br, 44.6. $C_6H_4O_4N_4Br_2$ requires C, 20.2; H, 1.1; N, 15.7; Br, 44.9%).

*2-Bromo-3-chloro-4:6-dinitrophenylhydrazine* was prepared similarly by taking an equivalent quantity of 1:3-dichloro-2-bromo-4:6-dinitrobenzene in place of 1:2:3-tribromo-4:6-dinitrobenzene. The phenylhydrazine was also slightly soluble in ethanol. It was crystallised from an excess of it in dirty yellow crystals (69%), m.p. 194°. (Found: C, 22.8; H, 1.2; N, 17.6; Br + Cl, 36.8. $C_6H_4O_4N_4BrCl$ requires C, 23.1; H, 1.3; N, 17.9; Br + Cl, 37.0%).

*Preparation of Phenylhydrazones.*—The hydrazones were obtained in nearly quantitative yields by refluxing for 4 to 5 minutes a mixture of the phenylhydrazine (0.5 g.) in ethanol (5 c.c.) and equimolecular proportions of the carbonyl compounds in presence of 1 to 2 drops of $H_2SO_4$ (conc.). These were purified by recrystallisation from an excess of ethanol or ethyl acetate. Characteristics of hydrazones prepared are recorded in Table I.

* All melting points recorded are uncorrected

TABLE I

| S. No. | Carbonyl compound. | 3:4-Dibromo-6-NP. M.P. | Colour. | Formula. | % Bromine. Found. | Calc. | 2:3-Dibromo-4:6-DNP. M.P. | Colour. | Formula. | % Bromine. Found. | Calc. | 2-Bromo-3-chloro-4:6-DNP. M.P. | Colour. | Formula. | % Br + Cl. Found. | Calc. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. | Acetone | 151° | Orange | $C_9H_9O_2N_2Br_2$ | 45.1 | 45.5 | 185° | Pale yellow | $C_9H_8O_4N_4Br_2$ | 40.2 | 40.4 | 141° | Lemon-yellow | $C_9H_8O_4N_4BrCl$ | 32.6 | 32.8 |
| 2. | Ethyl methyl ketone | 99° | Reddish orange | $C_{10}H_{11}O_2N_2Br_2$ | 43.7 | 43.8 | 99° | Lemon-yellow | $C_{10}H_{10}O_4N_4Br_2$ | 38.7 | 39.0 | 99° | Yellow | $C_{10}H_{10}O_4N_4BrCl$ | 31.5 | 31.6 |
| 3. | Acetophenone | 158° | Orange | $C_{14}H_{11}O_2N_2Br_2$ | 38.4 | 38.7 | 188° | Yellow | $C_{14}H_{10}O_4N_4Br_2$ | 34.8 | 34.9 | 188° | Canary-yellow | $C_{14}H_{10}O_4N_4BrCl$ | 27.4 | 2.79 |
| 4. | Benzaldehyde | 237° | Brick-red | $C_{13}H_9O_2N_2Br_2$ | 40.0 | 40.1 | 235° | Do | $C_{13}H_8O_4N_4Br_2$ | 35.8 | 36.0 | 221° | Do | $C_{13}H_8O_4N_4BrCl$ | 28.5 | 28.9 |
| 5. | Salicylaldehyde | 280° | Light orange | $C_{13}H_9O_3N_2Br_2$ | 38.4 | 38.5 | 221° | Yellowish orange | $C_{13}H_8O_6N_4Br_2$ | 34.6 | 34.7 | 225° | Light orange | $C_{13}H_8O_5N_4BrCl$ | 27.6 | 27.8 |
| 6. | *p*-Ethyl-acetophenone | 170° | Reddish orange | $C_{16}H_{15}O_2N_2Br_2$ | 36.0 | 36.2 | | | | | | | | | | |
| 7. | 2-Chloro-5-methylaceto-phenone | 161° | Yellowish orange | $C_{15}H_{12}O_2N_2Br_2Cl$ | Br&Cl 42.1 | Br&Cl 42.3 | | | | | | | | | | |
| 8. | 2: 5-Dichloro-acetophenone | 173° | Yellow | $C_{14}H_9O_2N_2Br_2Cl_2$ | Br & Cl 47.6 | Br & Cl 47.9 | | | | | | 204° | Yellow | $C_{14}H_8O_4N_4BrCl_2$ | 38.4 | 38.6 |
| 9. | *p*-Methyl-acetophenone | 122° | Yellowish orange | $C_{15}H_{12}O_2N_2Br_2$ | 37.2 | 37.4 | | | | | | | | | | |

NP denotes nitrophenylhydrazone.
DNP denotes dinitrophenylhydrazone.

One of the authors (H.G.G.) is thankful to the Govt. of India for the award of a scholarship.

CHEMICAL LABORATORY,
MEERUT COLLEGE, MEERUT.

*Received November* 13, 1959.

[Jour. Indian Chem. Soc., Vol. 37, No. 7, 1960]

# SYNTHESIS OF SOME SUBSTITUTED SULPHATHIAZOLES

BY A. B. SEN AND A. K. ROY

Seven different substituted 2-aminothiazoles have been prepared and condensed with acetylsulphanilyl chloride to obtain the corresponding sulphonamides in order to study their therapeutic activity.

Investigations for the synthesis of compounds related to sulphanilamide and for the study of their chemotherapeutic properties, with a view to overcoming some of the drawbacks of the drugs so far known (Goodman and Levy, *J. Amer. Med. Assoc.*, 1937, **109,** 1005; Bucy, *ibid.*, 1937, **109,** 1007), comprised mainly replacement of the amido-H by some other chain or group, mostly heterocyclic moiety. These led to the discovery of sulphathiazole, sulphadiazine and sulphaguanidine. That such replacements are expected to have a great therapeutic importance has also been stressed by several workers (Whitely, *Lancet*, 1937, *i*, 1517; Crossbey *et al.*, *J. Amer. Chem. Soc.*, 1938, **60,** 2217).

In view of the usefulness of the thiazole compounds in therapy (Bambas, *J. Amer. Chem. Soc.*, 1945, **67,** 671; Schaeffer and Toomey, *Amer. J. Med.*, 1945, **6,** 667; Bovet *et al.*, *Amer. Inst. Pasteur*, 1946, **72,** 105; Sondern and Breivogel, U.S.P. 2440703/1948), the authors considered worthwhile to undertake the preparation of substituted sulphathiazoles as a systematic study involving variation of substituents on the thiazolyl nucleus does not seem to have been undertaken.

The substituted 2-aminothiazoles were prepared from substituted hydroxyacetophenones, viz., 2-hydroxy-(5 methyl-, 4-methyl-, 4-ethyl-, 3-chloro-, 3:5-dichloro- and 3-chloro-4 methyl)-acetophenones, by treating with thiourea in the presence of iodine, following the method of King and Hlavacek (*J. Amer. Chem. Soc.*, 1950, **72,** 3722).

The required ketones were obtained by the Fries migration of the acetates of the corresponding phenols in the usual way. The acetates were prepared by following the method of Chattaway (*J. Chem. Soc.*, 1931, 2495).

The condensation of 2-aminothiazoles with acetylsulphanilyl chloride in pyridine (cf. D[illegible] and Rout, this *Journal*, 1955, **32,** 663) yielded the substituted 2-acetamidosulphonamides, which were also hydrolysed to the corresponding 2-amino compounds with 12% hydrochloric acid.

## EXPERIMENTAL

*2-Amino-4-p-chlorophenyl-5-methylthiazole.*—A mixture of *p*-chloropropiophenone (8.4 g.), thiourea (7.6 g.) and iodine (12.7 g.) was heated for 24 hours on the steam-bath, then cooled and extracted with ether to remove the unchanged ketone and iodine. The residue was extracted with boiling water and filtered. Ammonia was added to the filtrate and the solid separating was filtered and recrystallised from ethanol, m.p. 140°, yield 55%. (Found: S, 13.87. $C_{10}H_9N_2ClS$ requires S, 14.25%).

The other six thiazoles were prepared in the same way from the appropriate hydroxyacetophenones and were characterised through their acetyl derivatives, prepared in the usual way. The m.p., yields and analysis of the substituted 2-aminothiazoles and their acetyl derivatives are recorded in Table I.

TABLE I

| | 2-Aminothiazole. M.P. | % Yield. | % Sulphur. Found. | Calc. | Acetates M.P. | % Sulphur. Found. | Calc. |
|---|---|---|---|---|---|---|---|
| 4-*p*-Chlorophenyl 5-methyl-A | 140° | 55 | 13.87 | 14.25 | 235° | 11.63 | 12.00 |
| 4-(2-Hydroxy-5-methylphenyl)-A | 200° | 46 | 15.21 | 15.53 | 216° | 12.67 | 12.91 |
| 4-(2-Hydroxy-4-methylphenyl)-A | 175° | 42 | 15.23 | 15.53 | 195° | 12.73 | 12.91 |
| 4-(2-Hydroxy-4-ethylphenyl)-A | 132° | 52 | 14.23 | 14.54 | 153° | 11.87 | 12.21 |
| 4-(2-Hydroxy-3-chlorophenyl)-A | 207° | 39 | 13.86 | 14.21 | 241° | 11.67 | 11.91 |
| 4-(2-Hydroxy-3: 5-dichlorophenyl)-A | 117° | 25 | 12.03 | 12.26 | .. | .. | .. |
| 4-(2-Hydroxy-3-chloro-4-methylphenyl)-A | 185° | 48 | 12.95 | 13.30 | 261° | 11.21 | 11.32 |

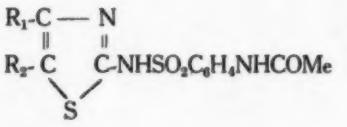
N.B. A denotes 2-aminothiazole.

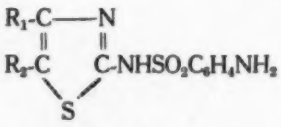
4-*p*-*Chlorophenyl*-5-*methyl*-2-(N⁴-*acetylsulphanilamido*)-*thiazole*.—4-*p*-Chlorophenyl-5-methyl-2-aminothiazole (1.9 g.) and *p*-acetamidobenzenesulphonyl chloride (2.3 g.) were treated with freshly distilled pyridine (15 c.c.). The mixture was heated on a water-bath at 65-70° for 2½ hours. After cooling, the mixture was diluted with water, when a precipitate was obtained. It was filtered, washed with water, and crystallised from ethanol, m.p. 295°, yield 58%. (Found: N, 9.58. $C_{18}H_{16}O_3N_3ClS_2$ requires N, 9.96%).

4-*p*-*Chlorophenyl*-5-*methyl*-2-*sulphanilamidothiazole*.—To the above compound (1 g.) 12% HCl (4 c.c.) was added and the mixture slowly refluxed for 2 hours. It was then poured into a beaker containing an equal volume of water, heated to boiling and filtered. The filtrate was cooled and solid sodium carbonate was added in small portions with continuous stirring until the solution was just alkaline to litmus. The precipitate formed was filtered, washed and crystallised from ethanol, m.p. 162° (decomp.), yield 30%. (Found: N, 10.95. $C_{16}H_{14}O_2N_3ClS_2$ requires N, 11.32%).

The m. p., yields and analytical data for the condensation products of *p*-acetamidobenzenesulphonyl chloride with other 2-aminothiazoles, and their corresponding amino compounds are shown in Table II.

TABLE II





| $R_1$. | $R_2$. | M.P. | %Yield. | % Nitrogen. Found. | Calc. | M.P. | %Yield. | % Nitrogen. Found. | Calc. |
|---|---|---|---|---|---|---|---|---|---|
| *p*-Chlorophenyl- | Me | 296° | 58 | 9.58 | 9.96 | 162° | 30 | 10.95 | 11.33 |
| 2-Hydroxy-5-methylphenyl- | H | 200° | 50 | 10.13 | 10.42 | .. | .. | .. | .. |
| 2-Hydroxy-4-methylphenyl- | H | 250° | 56 | 10.07 | 10.42 | 189° | 40 | 11.07 | 11.64 |
| 2-Hydroxy-4-ethylphenyl- | H | 152° | 55 | 9.83 | 10.07 | 144° | 45 | 11.16 | 11.30 |
| 2-Hydroxy-3-chlorophenyl- | H | 195° | 58 | 9.34 | 9.91 | .. | .. | .. | .. |
| 2-Hydroxy-3:5-dichlorophenyl- | H | 93° | 45 | 8.89 | 9.17 | .. | .. | .. | .. |
| 2-Hydroxy-3-chloro-4-methylphenyl- | H | 165° | 48 | 9.47 | 9.66 | 148° | 35 | 10.32 | 10.60 |

CHEMICAL LABORATORIES,
LUCKNOW UNIVERSITY, LUCKNOW.

*Received March 2, 1960.*

[Jour. Indian Chem. Soc., Vol. 37, No. 7, 1960]

# SYNTHESIS OF α/β -ARYL- AND γ -ARYL- γ -BENZYL- γ -BUTYROLACTONES

By D. K. Genge and J. J. Trivedi

Several γ-butyrolactones having methoxy and/or chloro-substituted aryl group on α/β position and aryl and benzyl groups on γ position have been synthesised.

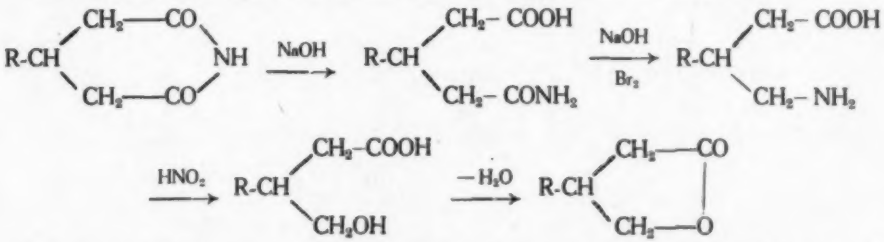
γ-Butyrolactones, synthesised by Rosenmund *et al.* (*Arch. Pharm.*, 1934, **272**, 313; *Chem. Ber.*, 1951, **84**, 711) and Nargund *et al.* (*J. Ind. Med. Assoc.*, 1945, **14**, 69,73), mainly possessed a substituted aryl group on γ position of the lactone ring. It would be interesting therefore to examine lactones possessing aryl group on α or β position.

α-Aryl-γ-butyrolactones have been synthesised by following the method of Carre and Liebermann (*Compt. rend.*, 1933, **196**, 117) from substituted benzyl cyanides as shown below :



In this way α-3-chloro-4-methoxy-, 2-methoxy-5-chloro-, 2:4-, 3:4- and 2:5-dichloro-phenyl-γ-butyrolactones were synthesised from the corresponding substituted benzyl cyanides.

β-Aryl-γ-butyrolactones were synthesised from β-arylglutarimides as shown below :



In this way β-3-chloro-4-methoxy-, 2-methoxy-5-chloro-, 2:4-, 3:4- and 2:5-dichloro-phenyl-γ-butyrolactones were prepared from the relatively substituted phenylglutarimides.

Trivedi and Nargund (*J. Univ. Bombay*, 1941, **10**, Part 3, 102) prepared γγ-disubstituted γ -butyrolactones by the action of alkylmagnesium bromide on ethyl β -aroylpropionates. γ-Benzyl-γ-aryl-γ-butyrolactones have been prepared by the condensation of benzylmagnesium halides with ethyl β-aroylpropionates.

## Experimental

*α-Aryl-γ-butyrolactones.*—Substituted benzyl cyanides were prepared from the corresponding aryl aldehydes through benzyl alcohols (Cross-Cannizzaro) and benzyl halides ($SOCl_2$).

*Condensation of Substituted Benzyl Cyanides with Ethylene Chlorhydrin and Preparation of α-Aryl-γ-butyrolactones.*—To the sodium salt of substituted benzyl cyanide (from cyanide 0.1 *M* and sodamide 0.1 *M*) in dry ether (75 c.c.) was added dry ethylene chlorhydrin (0.1 *M*) and the mixture was refluxed for 2 hours. The reaction mixture was then decomposed with ice and HCl and the resulting hydroxycyanide was heated with NaOH solution (20 g. in 50 c.c. water) for 4 hours. The solution was cooled, after removal of neutral impurities with ether, was washed, acidified with 25% $H_2SO_4$ and more of this added till its concentration reached 15% (approx.). It was then heated on a water-bath for 2 hours and the semisolid mass was kept over saturated

TABLE I

| | 2-Aminothiazole. M.P. | % Yield. | % Sulphur. Found. | Calc. | Acetates M.P. | % Sulphur. Found. | Calc. |
|---|---|---|---|---|---|---|---|
| 4-*p*-Chlorophenyl 5-methyl-A | 140° | 55 | 13.87 | 14.25 | 235° | 11.63 | 12.00 |
| 4-(2-Hydroxy-5-methylphenyl)-A | 200° | 46 | 15.21 | 15.53 | 216° | 12.67 | 12.91 |
| 4-(2-Hydroxy-4-methylphenyl)-A | 175° | 42 | 15.23 | 15.53 | 195° | 12.73 | 12.91 |
| 4-(2-Hydroxy-4-ethylphenyl)-A | 132° | 52 | 14.23 | 14.54 | 153° | 11.87 | 12.21 |
| 4-(2-Hydroxy-3-chlorophenyl)-A | 207° | 39 | 13.86 | 14.21 | 241° | 11.67 | 11.91 |
| 4-(2-Hydroxy-3: 5-dichlorophenyl)-A | 117° | 25 | 12.03 | 12.26 | .. | .. | .. |
| 4-(2-Hydroxy-3-chloro-4-methyl-phenyl)-A | 185° | 48 | 12.95 | 13.30 | 261° | 11.21 | 11.32 |

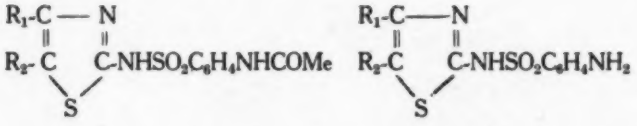
N.B. A denotes 2-aminothiazole.

4-p-*Chlorophenyl-5-methyl-2-*($N^4$-*acetylsulphanilamido)-thiazole.*—4-*p*-Chlorophenyl-5-methyl-2-aminothiazole (1.9 g.) and *p*-acetamidobenzenesulphonyl chloride (2.3 g.) were treated with freshly distilled pyridine (15 c.c.). The mixture was heated on a water-bath at 65-70° for 2½ hours. After cooling, the mixture was diluted with water, when a precipitate was obtained. It was filtered, washed with water, and crystallised from ethanol, m.p. 295°, yield 58%. (Found: N, 9.58. $C_{18}H_{16}O_3N_3ClS_2$ requires N, 9.96%).

4-p-*Chlorophenyl-5-methyl-2-sulphanilamidothiazole.*—To the above compound (1 g.) 12% HCl (4 c.c.) was added and the mixture slowly refluxed for 2 hours. It was then poured into a beaker containing an equal volume of water, heated to boiling and filtered. The filtrate was cooled and solid sodium carbonate was added in small portions with continuous stirring until the solution was just alkaline to litmus. The precipitate formed was filtered, washed and crystallised from ethanol, m.p. 162° (decomp.), yield 30%. (Found: N, 10.95. $C_{16}H_{14}O_2N_3ClS_2$ requires N, 11.32%).

The m. p., yields and analytical data for the condensation products of *p*-acetamidobenzenesulphonyl chloride with other 2-aminothiazoles, and their corresponding amino compounds are shown in Table II.

TABLE II




| $R_1$. | $R_2$. | M.P. | %Yield. | % Nitrogen. Found. | Calc. | M.P. | %Yield. | % Nitrogen. Found. | Calc. |
|---|---|---|---|---|---|---|---|---|---|
| *p*-Chlorophenyl- | Me | 296° | 58 | 9.58 | 9.96 | 162° | 30 | 10.95 | 11.33 |
| 2-Hydroxy-5-methylphenyl- | H | 200° | 50 | 10.13 | 10.42 | .. | .. | .. | .. |
| 2-Hydroxy-4-methylphenyl- | H | 250° | 56 | 10.07 | 10.42 | 189° | 40 | 11.07 | 11.64 |
| 2-Hydroxy-4-ethylphenyl- | H | 152° | 55 | 9.83 | 10.07 | 144° | 45 | 11.16 | 11.30 |
| 2-Hydroxy-3-chlorophenyl- | H | 195° | 58 | 9.34 | 9.91 | .. | .. | .. | .. |
| 2-Hydroxy-3:5-dichlorophenyl- | H | 93° | 45 | 8.89 | 9.17 | .. | .. | .. | .. |
| 2-Hydroxy-3-chloro-4-methylphenyl- | H | 165° | 48 | 9.47 | 9.66 | 148° | 35 | 10.32 | 10.60 |

CHEMICAL LABORATORIES,
LUCKNOW UNIVERSITY, LUCKNOW.

*Received March* 2, 1960.

[Jour. Indian Chem. Soc., Vol. 37, No. 7, 1960]

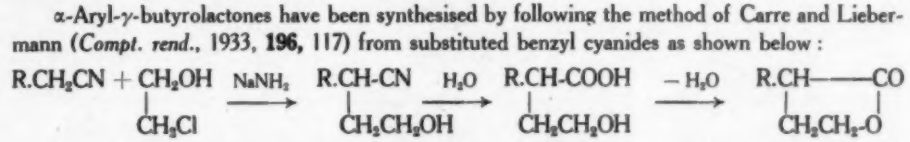
# SYNTHESIS OF α/β -ARYL- AND γ -ARYL- γ -BENZYL- γ -BUTYROLACTONES

By D. K. Genge and J. J. Trivedi

Several γ-butyrolactones having methoxy and/or chloro-substituted aryl group on α/β position and aryl and benzyl groups on γ position have been synthesised.

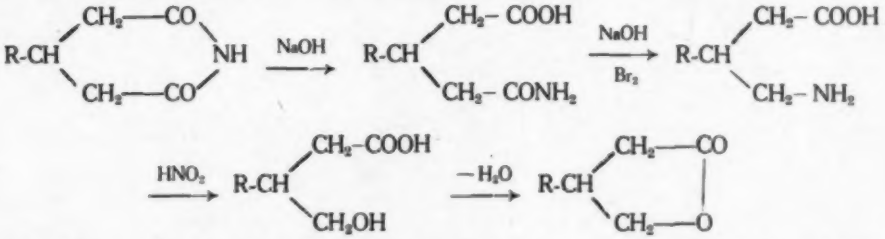
γ-Butyrolactones, synthesised by Rosenmund *et al.* (*Arch. Pharm.*, 1934, **272,** 313; *Chem. Ber.*, 1951, **84,** 711) and Nargund *et al.* (*J. Ind. Med. Assoc.*, 1945, **14,** 69,73), mainly possessed a substituted aryl group on γ position of the lactone ring. It would be interesting therefore to examine lactones possessing aryl group on α or β position.

α-Aryl-γ-butyrolactones have been synthesised by following the method of Carre and Liebermann (*Compt. rend.*, 1933, **196,** 117) from substituted benzyl cyanides as shown below :



In this way α-3-chloro-4-methoxy-, 2-methoxy-5-chloro-, 2:4-, 3:4- and 2:5-dichloro-phenyl-γ-butyrolactones were synthesised from the corresponding substituted benzyl cyanides.

β-Aryl-γ-butyrolactones were synthesised from β-arylglutarimides as shown below :



In this way β-3-chloro-4-methoxy-, 2-methoxy-5-chloro-, 2:4-, 3:4- and 2:5-dichloro-phenyl-γ-butyrolactones were prepared from the relatively substituted phenylglutarimides.

Trivedi and Nargund (*J. Univ. Bombay*, 1941, **10,** Part 3, 102) prepared γγ-disubstituted γ -butyrolactones by the action of alkylmagnesium bromide on ethyl β -aroylpropionates. γ-Benzyl-γ-aryl-γ-butyrolactones have been prepared by the condensation of benzylmagnesium halides with ethyl β-aroylpropionates.

## Experimental

*α-Aryl-γ-butyrolactones.*—Substituted benzyl cyanides were prepared from the corresponding aryl aldehydes through benzyl alcohols (Cross-Cannizzaro) and benzyl halides ($SOCl_2$).

*Condensation of Substituted Benzyl Cyanides with Ethylene Chlorhydrin and Preparation of α-Aryl-γ-butyrolactones.*—To the sodium salt of substituted benzyl cyanide (from cyanide 0.1 *M* and sodamide 0.1 *M*) in dry ether (75 c.c.) was added dry ethylene chlorhydrin (0.1 *M*) and the mixture was refluxed for 2 hours. The reaction mixture was then decomposed with ice and HCl and the resulting hydroxycyanide was heated with NaOH solution (20 g. in 50 c.c. water) for 4 hours. The solution was cooled, after removal of neutral impurities with ether, was washed, acidified with 25% $H_2SO_4$ and more of this added till its concentration reached 15% (approx.). It was then heated on a water-bath for 2 hours and the semisolid mass was kept over saturated

sodium bicarbonate solution for 24 hours. The insoluble lactone was purified by crystallisation, if solid, or distillation under reduced pressure, if liquid. The overall yield of lactones was 40%.

*β-Aryl-γ-butyrolactones.*—The required β-arylglutarimides were prepared as described by Trivedi *et al.* (this *Journal*, 1959, **36,** 677). Monoamide of β-arylglutaric acid was dissolved in NaOH (24 g. in 84 c.c. water) solution and to this was added 0.5 *N* sodium hypochlorite (180 c.c.) and the mixture was stirred mechanically for 3 hours. The solution was filtered and the filtrate was exactly neutralised with dilute hydrochloric acid when β-aryl-γ-aminobutyric acid separated. In the case of dihalo-compounds sodium hypobromite was used. To a solution of β-aryl-γ-aminobutyric acid (0.03 *M*) in 20% $H_2SO_4$ (40 c.c.) was added an ice-cooled solution of sodium nitrite (2.75 g., 20 c.c.) with vigorous stirring. It was then treated with an equal volume of 20% $H_2SO_4$ and the solution heated on a water-bath for an hour. The oily product was washed several times with sodium bicarbonate solution and the insoluble lactone was purified by distillation under reduced pressure. The yield of the lactone was 50%.

*γ-Aryl-γ-benzyl-γ-butyrolactones* were prepared by the action of benzylmagnesium chloride and *p*-methoxybenzylmagnesium bromide on ethyl β-aroylpropionic acids (Nargund *et al.*, this *Journal*, 1937, **14,** 406; *loc. cit.*) by the method described by Trivedi and Nargund (*loc. cit.*). Compounds prepared are shown in Tables I and II.

TABLE I

| No. | Compounds. | M.P. or B.P. & crystal shape. | Formula. | % Chlorine. Found. | Calc. |
|---|---|---|---|---|---|
| 1. | α-(3-Chloro-4-methoxyphenyl)-B | Yellow liquid, 130-35°/0.6 mm. | $C_{11}H_{11}O_3Cl$ | 15.8 *(230.0 | 15.7 226.5) |
| 2. | α-(2-Methoxy-5-chlorophenyl)-B | 128-29° | $C_{11}H_{11}O_3Cl$ | 15.4 (228.0 | 15.7 226.5) |
| 3. | α-(2:4-Dichlorophenyl)-B | 80° | $C_{10}H_8O_2Cl_2$ | 30.8 (235.0 | 30.7 232.0) |
| 4. | α-(3:4-Dichlorophenyl)-B | Yellow liquid, 185-89°/1 mm. | $C_{10}H_8O_2Cl_2$ | 30.5 (230.0 | 30.7 231.0) |
| 5. | α-(2:5-Dichlorophenyl)-B | Yellow liquid, 163-68°/1 mm. | $C_{10}H_8O_2Cl_2$ | 30.6 (231.0 | 30.7 231.0) |
| 6. | β-(3-Chloro-4-methoxyphenyl)-B | Yellow liquid, 208-13°/0.5 mm. | $C_{11}H_{11}O_3Cl$ | 15.9 (230.0 | 15.7 226.5) |
| 7. | β-(2-methoxy-5-chlorophenyl)-B | Yellow liquid, 158-63°/0.4 mm. | $C_{11}H_{11}O_3Cl$ | 15.5 (228.0 | 15.7 226.5) |
| 8. | β-(2:4-Dichlorophenyl)-B | 70° | $C_{10}H_8O_2Cl_2$ | 30.9 (234.0 | 30.7 231.0) |
| 9. | β-(3:4-Dichlorophenyl)-B | Yellow liquid, 185-90°/0.8 mm. | $C_{10}H_8O_2Cl_2$ | 30.5 (230.0 | 30.7 231.0) |
| 10. | β-(2:5-Dichlorophenyl)-B | Yellow liquid, 170-75°/0.8 mm. | $C_{10}H_8O_2Cl_2$ | 30.7 (232.0 | 30.7 231.0) |
| 11. | β-(3:4-Dichlorophenyl)-γ-AB | Granules from hot water; 204° | $C_{10}H_{11}O_2NCl_2$ | 28.9 (252.0 | 28.6 248.0) |
| 12. | β-(2:5-Dichlorophenyl)-γ-AB | Colorless needles from alcohol; 234° | $C_{10}H_{11}O_2NCl_2$ | 28.9 (250.0 | 28.6 248.0) |

B denotes butyrolactone and AB, aminobutyric acid.

* Figures in parenthesis relate to neutral equivalents.

TABLE II

| No. | Compounds. | M.P. or B.P. and crystal shape. | Formula. | Found. | | Calc. |
|---|---|---|---|---|---|---|
| 1. | 2-Methoxy-5-chlorobenzyl alcohol | Needles from alcohol, 58° | $C_8H_9O_2Cl$ | Cl: | 20.8 | 20.6 |
| 2. | 2:5-Dichlorobenzyl cyanide | Do, 83-84° | $C_8H_5NCl_2$ | N: | 7.7 | 7.5 |
| 3. | Ethyl β-(4-methoxy-3-methylbenzoyl) propionate | Do, 63° | $C_{14}H_{18}O_4$ | C: | 67.0 | 67.2 |
| | | | | H: | 7.0 | 7.2 |
| 4. | Ethyl β-(4-chlorobenzoyl)propionate | Do, 56° | $C_{12}H_{13}O_3Cl$ | Cl: | 15.0 | 14.8 |
| 5. | Monoamide of β-(3-chloro-4-mpthoxy-phenyl)-glutaric acid | Granules from hot water, 147° | $C_{12}H_{14}O_4NCl$ | Cl: | 13.3 | 13.1 |
| | | | | N.E. | 270.0 | 271.5 |
| 6. | Monoamide of β-(2-methoxy-5- chloro-phenyl)-glutaric acid | Colorless needles from hot water, 168° | $C_{12}H_{14}O_4NCl$ | Cl: | 13.3 | 13.1 |
| | | | | N.E. | 274.0 | 271.5 |
| 7. | Monoamide of β-(3:4-dichlorophenyl)-glutaric acid | Do, 199° | $C_{11}H_{11}O_3NCl_2$ | Cl: | 25.9 | 25.7 |
| | | | | N.E. | 27.5 | 276.0 |
| 8. | Monoamide of β-(2:5-dichlorophenyl)-glutaric acid | Granules from hot water, 180° | $C_{11}H_{11}O_3NCl_2$ | Cl: | 25.9 | 25.7 |
| | | | | N.E. | 278.0 | 276.0 |
| 9. | β-(3-Chloro-4-methoxyphenyl)-γ-aminobutyric acid | Colorless needles from hot water, 132° | $C_{11}H_{14}O_3NCl$ | Cl: | 14.8 | 14.6 |
| | | | | N.E. | 245.0 | 243.5 |
| 10. | β-(2-Methoxy-5-chlorophenyl)-γ-aminobutyric acid | Do, 175° | $C_{11}H_{14}O_3NCl$ | Cl: | 14.5 | 14.6 |
| | | | | N.E. | 244.0 | 243.5 |
| 11. | γ-(Methoxyphenyl) γ-(benzyl)-γ-butyrolactone | Do, from dilute alcohol, 87° | $C_{18}H_{18}O_3$ | C: | 76.8 | 76.6 |
| | | | | H: | 6.6 | 6.4 |
| | | | | N.E. | 285.0 | 282.0 |
| 12. | γ-(4-Methoxy-3-methylphenyl)-γ-(benzyl)- γ-butyrolactone | Do, 140° | $C_{19}H_{20}O_3$ | C: | 77.2 | 77.0 |
| | | | | H: | 6.9 | 6.8 |
| | | | | N.E. | 299.0 | 296.0 |
| 13. | γ-(2:4-Dimethoxyphenyl)- γ-(benzyl)-γ-butyrolactone | Do, 137° | $C_{19}H_{20}O_4$ | C: | 73.2 | 73.0 |
| | | | | H: | 6.6 | 6.4 |
| | | | | N.E. | 314.0 | 312.0 |
| 14. | γ-(3:4-Dimethoxyphenyl)-γ -(benzyl)-γ-butyrolactone | Yellow liquid, 198-203°/1 mm | $C_{19}H_{20}O_4$ | C: | 72.2 | 73.0 |
| | | | | H: | 6.6 | 6.4 |
| | | | | N.E. | 316.0 | 312.0 |
| 15. | γ-(2:5-Dimethoxyphenyl)-γ-(benzyl)-γ-butyrolactone | Colorless needles from dilute alcohol, 94° | $C_{19}H_{20}O_4$ | C: | 73.2 | 73.0 |
| | | | | H: | 6.5 | 6.4 |
| | | | | N.E. | 315.0 | 312.0 |
| 16. | γ-(p-Chlorophenyl)-γ-(benzyl)-γ-butyrolactone | Do, 90° | $C_{17}H_{15}O_3Cl$ | Cl: | 12.6 | 12.4 |
| | | | | N.E. | 289.0 | 286.5 |
| 17. | γ-(p-Methoxyphenyl)-γ- (p-methoxy-benzyl)-γ-butyrolactone | Yellow liquid, 140-45°/0.3 mm. $n^{26}D$ 1.54° | $C_{19}H_{20}O_4$ | C: | 73.3 | 73.1 |
| | | | | H: | 6.6 | 6.4 |
| | | | | N.E. | 315.0 | 312.0 |
| 18. | γ-(4-Methoxy-3-methylphenyl)-γ-(p-methoxybenzyl)-γ-butyrolactone | Yellow liquid, 189-93°/1 mm $n^{26}D$ 1.540 | $C_{20}H_{22}O_4$ | C: | 73.8 | 73.6 |
| | | | | H: | 6.9 | 6.7 |
| | | | | N.E. | 328.0 | 326.0 |
| 19. | γ-(2:4-Dimethoxyphenyl)-γ-(p-methoxybenzyl)-γ-butyrolactone | Yellow liquid, 181-85°/0.9 mm $n^{26}D$ 1.543 | $C_{20}H_{22}O_5$ | C: | 70.3 | 70.2 |
| | | | | H: | 6.6 | 6.4 |
| | | | | N.E. | 346.0 | 342.0 |
| 20. | γ-(3:4-Dimethoxyphenyl)-γ-(p-methoxybenzyl)-γ-butyrolactone | Yellow liquid, 130-35/0.8 mm $n^{26}D$ 1.529 | $C_{20}H_{22}O_5$ | C: | 70.3 | 70.2 |
| | | | | H: | 6.4 | 6.4 |
| | | | | N.E. | 346.0 | 342.0 |
| 21. | γ-(2:5-Dimethoxyphenyl)-γ-(p-methoxybenzyl)-γ-butyrolactone | Yellow liquid, 183-87°/0.7 mm $n^{26}D$ 1.535 | $C_{20}H_{22}O_5$ | C: | 70.1 | 70.2 |
| | | | | H: | 6.6 | 6.4 |
| | | | | N.E. | 344.0 | 342.0 |

The authors thank Dr. R. D. Desai for interest in the work and the Ahmedabad Education Society for defraying the expenses incurred during the course of this work, and the Government of India for a research grant to one of them (J.J.T.).

CHEMISTRY DEPARTMENT,
M. G. SCIENCE INSTITUTE,
AHMEDABAD-9.

*Received February* 18, 1960

[Jour. Indian Chem. Soc., Vol. 37, No. 7, 1960]

# 4-(SUBSTITUTED) BENZYLTHIOSEMICARBAZONES

BY P. R. PATHAN AND J. J. TRIVEDI

4-Substituted benzylthiosemicarbazones have been prepared by the action of 4-(substituted) benzylthiosemicarbazides on aryl aldehydes.

Following the discovery of the tuberculostatic activity of *p*-acetamidobenzaldehyde thiosemicarbazone by Domagk *et al.* (*Naturwiss.*, 1946, **33**, 315) a large number of thiosemicarbazones of aryl and hetero aldehydes and ketones have been prepared. 4-Chloro- and 4-bromo-benzylthioureas have been reported to show tuberculostatic activity (Mrs. Shah, Ph. D. thesis, Bombay Univ., 1957). This observation prompted us to prepare thiosemicarbazones containing a substituted benzyl group. 4-(Substituted) benzylthiosemicarbazones have been prepared by the condensation of 4-(substituted) benzylthiosemicarbazides with aromatic aldehydes.

## EXPERIMENTAL

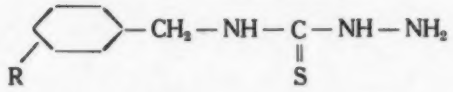
4-(Substituted) benzylthiosemicarbazides were prepared by the action of benzyl *iso*thiocyanates (Trivedi *et al.*, this *Journal*, 1956, **33**, 423; 1958, **35**, 658) on hydrazine hydrate in cold (Buu Hoï *et al.*, *J. Chem. Soc.*, 1956, 2160).

4-(*Substituted*) *benzylthiosemicarbazones* were prepared by the action of 4-(substituted) benzylthiosemicarbazides on aromatic aldehydes in ethanolic solution (Buu Hoï *et al.*, *loc. cit.*).

All the compounds were crystallised from dilute ethanol.

### TABLE I

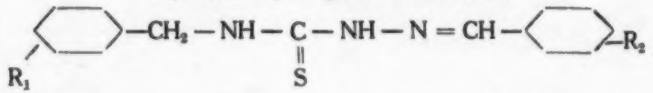
4-(*Substituted*) *benzylthiosemicarbazides.*




| No. | R. | M.P. | Formula. | % Sulphur. Found. | Calc. |
|---|---|---|---|---|---|
| 1. | *o*-Chloro | 141° | $C_9H_{10}N_3ClS$ | 15.0 | 14.9 |
| 2. | *p*-Chloro | 156° | $C_9H_{10}N_3ClS$ | 14.9 | 14.9 |
| 3. | *p*-Bromo | 135° | $C_9H_{10}N_3BrS$ | 12.4 | 12.3 |
| 4. | *o*-Methyl | 152° | $C_9H_{13}N_3S$ | 16.3 | 16.4 |
| 5. | *m*-Methyl | 106° | $C_9H_{13}N_3S$ | 16.3 | 16.4 |
| 6. | *p*-Methyl | 156° | $C_9H_{13}N_3S$ | 16.5 | 16.4 |
| 7. | 2: 4-Dimethyl | 129° | $C_{10}H_{15}N_3S$ | 15.2 | 15.3 |
| 8. | 3: 4-Dimethyl | 176° | $C_{10}H_{15}N_3S$ | 15.4 | 15.3 |
| 9. | 2: 5-Dimethyl | 181° | $C_{10}H_{15}N_3S$ | 15.4 | 15.3 |

## TABLE II

*4-(Substituted) benzylthiosemicarbazones.*



| $R_2$. | M.P. | Formula. | % Sulphur. Found. | Calc. | M.P. | Formula. | % Sulphur Found. | Calc. | M.P. | Formula. | % Sulphur. Found. | Calc. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | $R_1$ = o-Chloro. | | | | $R_1$ = p-Chloro. | | | | $R_1$ = p-Bromo- | |
| H | 178° | $C_{16}H_{14}N_3ClS$ | 10.6 | 10.5 | 151° | $C_{16}H_{14}N_3ClS$ | 10.5 | 10.5 | 138° | $C_{16}H_{14}N_3BrS$ | 9.1 | 9.2 |
| o-OH | 199° | $C_{16}H_{14}ON_3ClS$ | 10.1 | 10.0 | 192° | $C_{16}H_{14}ON_3ClS$ | 10.0 | 10.0 | 185° | $C_{16}H_{14}ON_3SBr$ | 8.8 | 8.8 |
| p-OMe | 168° | $C_{16}H_{16}ON_3ClS$ | 9.6 | 9.6 | 170° | $C_{16}H_{16}ON_3ClS$ | 9.7 | 9.6 | 129° | $C_{16}H_{16}ON_3BrS$ | 8.6 | 8.5 |
| o-Cl | 195° | $C_{16}H_{13}N_3Cl_2$ | 9.6 | 9.5 | 145° | $C_{16}H_{13}N_3Cl_2S$ | 9.5 | 9.5 | 147° | $C_{16}H_{13}N_3BrClS$ | 8.5 | 8.4 |
| p-Cl | 184° | $C_{16}H_{13}N_3Cl_2S$ | 9.5 | 9.5 | 165° | $C_{16}H_{13}N_3Cl_2S$ | 9.6 | 9.5 | 151° | $C_{16}H_{13}N_3BrClS$ | 8.5 | 8.4 |
| 2: 4-$Cl_2$ | 209° | $C_{16}H_{12}N_3Cl_3S$ | 8.7 | 8.6 | 175° | $C_{16}H_{12}N_3Cl_3S$ | 8.7 | 8.6 | 185° | $C_{16}H_{12}N_3BrCl_2S$ | 7.8 | 7.7 |
| p-OH | 220° | $C_{16}H_{14}ON_3ClS$ | 10.0 | 10.0 | 220° | $C_{16}H_{14}ON_3ClS$ | 10.0 | 10.0 | 209° | $C_{16}H_{14}ON_3BrS$ | 8.9 | 8.8 |
| p-$(CH_3)_2N$ | 166° | $C_{17}H_{19}N_4ClS$ | 9.3 | 9.2 | 174° | $C_{17}H_{19}N_4ClS$ | 9.3 | 9.2 | 162° | $C_{17}H_{19}N_4BrS$ | 8.3 | 8.2 |
| | | $R_1$ = o-Me. | | | | $R_1$ = m-Me. | | | | $R_1$ = p-Me. | | |
| H | 132° | $C_{16}H_{17}N_3S$ | 11.4 | 11.3 | 113° | $C_{16}H_{17}N_3S$ | 11.4 | 11.3 | 132° | $C_{16}H_{17}N_3S$ | 11.4 | 11.3 |
| o-OH | 181° | $C_{16}H_{17}ON_3S$ | 10.7 | 10.7 | 152° | $C_{16}H_{17}ON_3S$ | 10.7 | 10.7 | 201° | $C_{16}H_{17}ON_3S$ | 10.7 | 10.7 |
| p-OMe | 150° | $C_{17}H_{19}ON_3S$ | 10.2 | 10.2 | 166° | $C_{17}H_{19}ON_3S$ | 10.3 | 10.2 | 168° | $C_{17}H_{19}ON_3S$ | 10.3 | 10.2 |
| o-Cl | 178° | $C_{16}H_{16}N_3ClS$ | 10.2 | 10.1 | 155° | $C_{16}H_{16}N_3ClS$ | 10.2 | 10.1 | 172° | $C_{16}H_{16}N_3ClS$ | 10.2 | 10.1 |
| p-Cl | 175° | $C_{16}H_{16}N_3ClS$ | 10.1 | 10.1 | 158° | $C_{16}H_{16}N_3ClS$ | 10.1 | 10.1 | 173° | $C_{16}H_{16}N_3ClS$ | 10.1 | 10.1 |
| 2: 4-$Cl_2$ | 209° | $C_{16}H_{15}N_3Cl_2S$ | 9.2 | 9.1 | 166° | $C_{16}H_{15}N_3Cl_2S$ | 9.2 | 9.1 | 177° | $C_{16}H_{15}N_3Cl_2S$ | 9.2 | 9.1 |
| p-OH | 196° | $C_{16}H_{17}ON_3S$ | 10.8 | 10.7 | 162° | $C_{16}H_{17}ON_3S$ | 10.8 | 10.7 | 215° | $C_{16}H_{17}ON_3S$ | 10.8 | 10.7 |
| p-$(CH_3)_2N$ | 149° | $C_{18}H_{22}N_4S$ | 9.8 | 9.8 | 105° | $C_{18}H_{22}N_4S$ | 9.9 | 9.8 | 150° | $C_{18}H_{22}N_4S$ | 9.7 | 9.8 |

TABLE II—*contd.*

| $R_2$. | Formula. | M.P. | % Sulphur. Found. | Calc. | M.P. | % Sulphur. Found. | Calc. | M.P. | % Sulphur. Found. | Calc. |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | $R_1$ = 3:4-Dimethyl. | | | $R_1$ = 2:4-Dimethyl. | | | $R_1$ = 2:5-Dimethyl. | |
| H | $C_{17}H_{19}N_3S$ | 121° | 10.7 | 10.8 | 182° | 10.9 | 10.8 | 125° | 10.9 | 10.8 |
| *o*-OH | $C_{17}H_{19}ON_3S$ | 171° | 10.3 | 10.2 | 207° | 10.3 | 10.2 | 201° | 10.3 | 10.2 |
| *p*-OMe | $C_{18}H_{21}ON_3S$ | 142° | 9.8 | 9.8 | 161° | 9.9 | 9.8 | 141° | 9.8 | 9.8 |
| *o*-Cl | $C_{17}H_{18}N_3ClS$ | 184° | 9.8 | 9.7 | 150° | 9.7 | 9.7 | 184° | 9.8 | 9.7 |
| *p*-Cl | $C_{17}H_{18}N_3ClS$ | 143° | 9.8 | 9.7 | 188° | 9.8 | 9.7 | 175° | 9.7 | 9.7 |
| 2:4-$Cl_2$ | $C_{17}H_{17}N_3Cl_2S$ | 185° | 8.8 | 8.7 | 208° | 8.8 | 8.7 | 200° | 8.8 | 8.7 |
| *p*-OH | $C_{17}H_{19}ON_3S$ | 164° | 10.2 | 10.2 | 205° | 10.3 | 10.2 | 206° | 10.2 | 10.2 |
| *p*-$(CH_3)_2N$ | $C_{19}H_{24}N_4S$ | 175° | 9.5 | 9.4 | 175° | 9.5 | 9.4 | 146° | 9.5 | 9.4 |

The authors thank Dr. R. D. Desai for interest in the work and the Ahmedabad Education Society for defraying the expenses incurred during the course of this work, and the Gujarat University for a research grant to one of them (J.J.T.).

CHEMISTRY DEPARTMENT,
M. G. SCIENCE INSTITUTE,
AHMEDABAD-9.

*Received April* 9, 1960.

[Jour. Indian Chem. Soc., Vol. 37, No. 7, 1960]

# THIAZOLIDONES. PART V. SYNTHESIS OF 5-ALKYL/BENZYL-2-ARYLIMINO-4-THIAZOLIDONES

By B. K. Raval and J. J. Trivedi

α-Bromo-fatty acids and α-bromo-β-phenylpropionic acid have been condensed with arylthioureas to yield the title compounds.

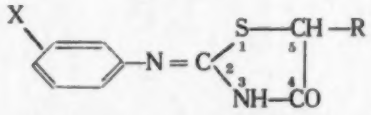
α-Bromo-fatty acids (from propionic, butyric[n] and caproic[n] acids) have been condensed with arylthioureas in presence of sodium acetate to yield 5-methyl/ethyl/butyl[n]-2-arylimino-4-thiazolidones. In order to obtain thiazolidones with a benzyl group on $C_5$, α-bromo-β-phenylpropionic acid has been condensed with arylthioureas, yielding 5-benzyl-2-arylimino-4-thiazolidones.

## Experimental

Substituted phenylthioureas were prepared from the corresponding amines. α-Bromo-fatty acids were prepared by bromination of propionic, butyric[n] and caproic[n] acids (Vogel, "Practical Organic Chemistry", 1951, p. 421). α-Bromo-β-phenylpropionic acid was prepared as described in "Org. Syn." (1941, **21**, 99).

Condensation of substituted phenylthioureas with α-bromo-fatty acids and α-bromo-β-phenylpropionic acid was carried out as described by Raval and Trivedi (this *Journal*, 1959, **36**, 733). Thiazolidones (yields about 60%) were crystallised from ethanol (Table I).

Table I




*5-Alkyl/benzyl-2-arylimino-4-thiazolidones.*

| No. | R. | X. | M.P. | Formula. | % Sulphur. Found. | Calc. |
|---|---|---|---|---|---|---|
| 1. | Me | *o*-Cl | 128° | $C_{10}H_9ON_2ClS$ | 12.8 | 13.0 |
| 2. | ,, | *p*-Br | 165° | $C_{10}H_9ON_2BrS$ | 11.0 | 11.2 |
| 3. | ,, | *m*-$CH_3$ | 294° | $C_{11}H_{12}ON_2S$ | 14.3 | 14.5 |
| 4. | ,, | 2:4-DiCl | 184° | $C_{10}H_8ON_2Cl_2S$ | 11.6 | 11.6 |
| 5. | ,, | 2:5-DiCl | 294° | ,, | 11.4 | ,, |
| 6. | ,, | 3:4-DiCl | 174° | ,, | 11.8 | ,, |
| 7. | ,, | *p*-*n*-$OC_6H_{13}$ | 225° | $C_{18}H_{27}O_2N_2S$ | 10.4 | 10.5 |
| *8. | Et | H | 154° | $C_{11}H_{12}ON_2S$ | 14.6 | 14.5 |
| 9. | ,, | *o*-Cl | 125° | $C_{11}H_{11}ON_2ClS$ | 12.4 | 12.6 |
| 10. | ,, | *m*-Cl | 144° | $C_{11}H_{11}ON_2ClS$ | 12.8 | 12.6 |
| 11. | ,, | *p*-Cl | 154° | ,, | 12.5 | ,, |
| 12. | ,, | *p*-Br | 148° | $C_{11}H_{11}ON_2BrS$ | 10.5 | 10.7 |
| 13. | ,, | *m*-$CH_3$ | 104° | $C_{12}H_{14}ON_2S$ | 13.8 | 13.7 |

* Dixon, *J. Chem. Soc.*, 1897, **71**, 635, records m.p. 148-49°.

TABLE I—*contd.*

| No. | R. | X. | M.P. | Formula. | % Sulphur. Found. | Calc. |
|---|---|---|---|---|---|---|
| 14. | ,, | *p*-$CH_3$ | 140° | $C_{13}H_{14}ON_2S$ | 13.5 | 13.7 |
| 15. | ,, | 2:4-DiCl | 130° | $C_{11}H_{10}ON_2Cl_2S$ | 10.8 | 11.0 |
| 16. | ,, | 2:5-DiCl | 154° | ,, | 11.0 | ,, |
| 17. | ,, | 3:4-DiCl | 132° | ,, | 11.2 | ,, |
| 18. | ,, | *p*-*n*-$OC_6H_{13}$ | 100° | $C_{17}H_{24}O_2N_2S$ | 10.2 | 10.0 |
| 19. | *n*-Bu | H | 144° | $C_{13}H_{16}ON_2S$ | 13.1 | 12.9 |
| 20. | ,, | *m*-Cl | 115° | $C_{13}H_{15}ON_2ClS$ | 11.2 | 11.3 |
| 21. | ,, | *p*-Cl | 136° | ,, | 11.4 | ,, |
| 22. | ,, | *p*-Br | 136° | $C_{13}H_{15}ON_2BrS$ | 10.0 | 9.8 |
| 23. | ,, | *m*-$CH_3$ | 98° | $C_{14}H_{18}ON_2S$ | 12.1 | 12.2 |
| 24. | ,, | *p*-$CH_3$ | 136° | ,, | 12.4 | ,, |
| 25. | ,, | *o*-$OCH_3$ | 118° | $C_{14}H_{18}O_2N_2S$ | 11.7 | 11.5 |
| 26. | ,, | 2:4-DiCl | 104° | $C_{13}H_{14}ON_2Cl_2S$ | 10.0 | 10.1 |
| 27. | ,, | 3:4-DiCl | 144° | ,, | 9.9 | ,, |
| 28. | -$CH_2$Ph | H | 183° | $C_{16}H_{14}ON_2S$ | 11.4 | 11.3 |
| 29. | ,, | *o*-Cl | 149° | $C_{16}H_{13}ON_2ClS$ | 10.0 | 10.1 |
| 30. | ,, | *m*-Cl | 163° | ,, | 10.2 | ,, |
| 31. | ,, | *p*-Cl | 212° | $C_{16}H_{13}ON_2ClS$ | 10.3 | 10.1 |
| 32. | ,, | *p*-Br | 217° | $C_{16}H_{13}ON_2BrS$ | 9.0 | 8.9 |
| 33. | ,, | *m*-$CH_3$ | 128° | $C_{17}H_{16}ON_2S$ | 10.9 | 10.8 |
| 34. | ,, | *o*-$OCH_3$ | 138° | $C_{17}H_{16}O_2N_2S$ | 10.4 | 10.3 |
| 35. | ,, | *p*-$OCH_3$ | 187° | ,, | 10.1 | ,, |
| 36. | ,, | 2:4-DiCl | 138° | $C_{16}H_{12}ON_2Cl_2S$ | 9.0 | 9.1 |
| 37. | ,, | 2:5-DiCl | 206° | ,, | 9.2 | ,, |
| 38. | ,, | 3:4-DiCl | 218° | ,, | 9.3 | ,, |
| 39. | ,, | *o*-COOEt | 167° | $C_{19}H_{18}O_3N_2S$ | 9.2 | 9.0 |
| 40. | ,, | *p*-*n*-$OC_3H_7$ | 161° | $C_{18}H_{20}O_2N_2S$ | 9.6 | 9.4 |
| 41. | ,, | *p*-*n*-$OC_6H_{13}$ | 141° | $C_{22}H_{26}O_2N_2S$ | 8.2 | 8.4 |

The authors thank Dr. R. D. Desai for interest in the work and the Ahmedabad Education Society for defraying the expenses incurred during the course of this work, and the Government of India for a research grant to one of them (J.J.T.).

CHEMISTRY DEPARTMENT,
M. G. SCIENCE INSTITUTE,
AHMEDABAD-9.

*Received March 7, 1960.*

[Jour. Indian Chem. Soc., Vol. 37, No. 7, 1960]

# POTENTIAL LOCAL ANAESTHETICS. PART I. SYNTHESIS OF BASIC *N*-BENZYLACETAMIDES

BY MISS S. L. DALAL AND J. J. TRIVEDI

*N*-(subst. benzyl)-chloroacetamides have been condensed with secondary amines to yield dialkylamino-, morpholinyl- and piperidinyl-*N*-(subst. benzyl)-acetamides.

Basic anilides in a large number have been sythesised, and amongst these diethylamino-2:6-dimethylacetanilide, Xylocaine, is the best known local anaesthetic (Lofgren and Lundquist, U.S.P. 2, 441,498/1948; *Chem. Abst.*, 1948, **42,** 6378).

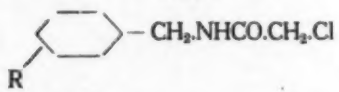
Benzyl alcohol possesses local anaesthetic properties (Maeht, *J. Pharmacol. Expt. Therap.*, 1918, **11,** 263) and *N*-benzyl-β-chloropropionamide shows anticonvulsant properties (Kushner *et al., J. Org. Chem.*, 1951, **16,** 1283). It was therefore thought of interest to prepare basic amides containing benzyl group. With this object in view dialkylamino-, morpholinyl- and piperidinyl-*N*-benzylacetamides have been prepared and described in this communication. Chloroacetyl chloride was allowed to react with benzylamines and the chloroacetyl-*N*-benzylamides were heated with secondary amines to yield the required basic amides. Hydrochlorides of compounds: (1) diethylamino-*N*-(*m*-methylbenzyl)-, (2) diethylamino-*N*-(*p*-methylbenzyl)- and (3) diethylamino-*N*-(*o*-chlorobenzyl)-acetamides (compounds No. 2, 3 and 4 respectively of Table II) were examined for local anaesthetic properties by the intra-dermal anaesthesia method of Bülbring and Wajda (*J. Pharmacol.*, 1945, **85,** 78) and were found to be active at 0.05% concentration.

## EXPERIMENTAL

Benzylamines were prepared from the corresponding benzyl halides by the method of Graymore (*J. Chem. Soc.*, 1945, 293; 1947, 1116).

*Condensation of Benzylamines with Chloroacetyl Chloride.*—To the amine (1 g.), suspended in water (5 c.c.) and cooled in an ice-salt mixture, were added dropwise with vigorous shaking chloroacetyl chloride and NaOH (10%, 5 c.c.) simultaneously. After allowing the reaction mixture to attain room temperature, the precipitate was filtered and washed with cold water, HCl (1:1), and finally with water. The substances crystallised in needles from dilute ethanol (Table I).

TABLE I

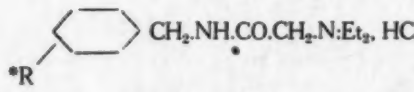



*N-Benzy-lchloroacetamides.*

| S. No. | R. | M.P. | Formula. | % Chlorine. Found. | Calc. |
|---|---|---|---|---|---|
| 1 | *o*-Me | 95° | $C_{10}H_{12}ONCl$ | 17.8 | 18.0 |
| 2 | *m*-Me | 48° | $C_{10}H_{12}ONCl$ | 17.9 | 18.0 |
| 3 | *p*-Me | 85° | $C_{10}H_{12}ONCl$ | 17.8 | 18.0 |
| 4 | *o*-Cl | 125° | $C_9H_9ONCl_2$ | 32.4 | 32.6 |
| 5 | *m*-Cl | 64-65° | $C_9H_9ONCl_2$ | 32.8 | 32.6 |
| 6 | *p*-Cl | 75° | $C_9H_9ONCl_2$ | 32.7 | 32.6 |
| 7 | 3:4-Dimethyl | 88° | $C_{11}H_{14}ONCl$ | 16.8 | 16.8 |
| 8 | 2:4-Dimethyl | 96° | $C_{11}H_{14}ONCl$ | 16.9 | 16.8 |
| 9 | 2:5-Dimethyl | 106° | $C_{11}H_{14}ONCl$ | 16.7 | 16.8 |

*Condensation of Secondary Amines with* N-*Benzyl-chloroacetamide.*—A mixture of *N*-benzyl-chloroacetamide (0.015 *M*) and secondary amine (0.03 *M*) in absolute ethanol (20 c.c.) was refluxed for 4 hours. Alcohol was distilled off and the residue was treated with a saturated $NaHCO_3$ solution, and the thick oily mass was dissolved in dilute HCl, filtered and treated with $NH_4OH$ solution to liberate the base. The oily base was extracted with ether, dried and converted into the hydrochloride (by passing dry HCl gas into dry ethereal solution). The hydrochlorides crystallised in needles from acetone. The compounds prepared are shown in Tables II, III and IV.

TABLE II

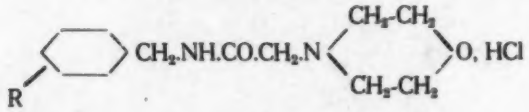



*Hydrochlorides of diethylamino*-N-(*subst.-benzyl*)-*acetamides.*

| S. No. | M.P. | Formula. | % Nitrogen. Found. | Calc. |
|---|---|---|---|---|
| 1 | 200° | $C_{14}H_{22}ON_2.HCl$ | 10.2 | 10.4 |
| 2 | 220° | $C_{14}H_{22}ON_2.HCl$ | 10.3 | 10.4 |
| 3 | 185° | $C_{14}H_{22}ON_2.HCl$ | 10.6 | 10.4 |
| 4 | 170° | $C_{13}H_{19}ON_2Cl.HCl$ | 9.4 | 9.6 |
| 5 | 195° | $C_{13}H_{19}ON_2Cl.HCl$ | 9.5 | 9.6 |
| 6 | 210° | $C_{13}H_{19}ON_2Cl.HCl$ | 9.5 | 9.6 |
| 7 | 205° | $C_{15}H_{25}ON_2.HCl$ | 9.7 | 9.8 |
| 8 | 195° | $C_{15}H_{25}ON_2.HCl$ | 9.6 | 9.8 |
| 9 | 130° | $C_{15}H_{25}ON_2.HCl$ | 9.9 | 9.8 |

* R serially same as in Table I.

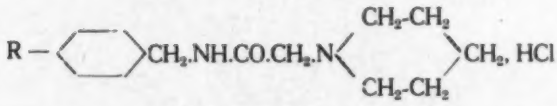
TABLE III




*Hydrochlorides of morpholinyl*-N-(*subst.-benzyl*)-*acetamides.*

| S. No. | R. | M.P. | Formula. | % Nitrogen. Found. | Calc. |
|---|---|---|---|---|---|
| 1 | *o*-Me | 210° | $C_{14}H_{20}O_2N_2.HCl$ | 10.0 | 9.8 |
| 2 | *m*-Me | 160° | $C_{14}H_{20}O_2N_2.HCl$ | 9.9 | 9.8 |
| 3 | *p*-Me | 280° | $C_{14}H_{20}O_2N_2.HCl$ | 9.7 | 9.8 |
| 4 | *o*-Cl | 180° | $C_{13}H_{17}O_2N_2Cl.HCl$ | 9.2 | 9.2 |
| 5 | *p*-Cl | 240° | $C_{13}H_{17}O_2N_2Cl.HCl$ | 9.0 | 9.2 |

TABLE IV



*Hydrochlorides of piperidinyl-N-(subst.-benzyl)-acetamides.*

| S. No. | R. | M.P. | Formula. | % Nitrogen. Found. | Calc. |
|---|---|---|---|---|---|
| 1 | *p*-Me | 202° | $C_{15}H_{22}ON_2.HCl$ | 10.0 | 9.9 |
| 2 | *o*-Cl | 110° | $C_{14}H_{19}ON_2Cl.HCl$ | 9.2 | 9.2 |

The authors thank Dr. R. D. Desai for the interest in the work and the Ahmedabad Education Society for defraying the expenses incurred during the course of this work, and Shri V. B. Desai of L. M. College of Pharmacy, Ahmedabad, for pharmacological testing.

DEPARTMENT OF CHEMISTRY,
M. G. SCIENCE INSTITUTE,
AHMEDABAD-9.

*Received December 7, 1959.*

[Jour. Indian Chem. Soc., Vol. 37, No. 7, 1960]

# SHORT NOTES

## SWIETENINE, THE NON-BITTER PRINCIPLE OF THE SEEDS OF *SWIETENIA MACROPHYLLA* KING

By S. Ghosh, T. Chakrabartty and Mrs. A. Chatterjee

*Swietenia macrophylla* King (Fam. *Meliaceae*) contains in its seeds a neutral non-bitter principle, swietenine and a bitter component, swietenolide. Earlier it was demonstrated by the present investigators that swietenine, m.p. 260° (decomp), $[\alpha]_D^{20°}$ -168° (chloroform) was an $\alpha\beta$-unsaturated lactone (which can be opened reversibly) having a tertiary hydroxyl, a six-ring ketone and a methoxyl group (Chakrabartty and Chatterjee, this *Journal*, 1957, **34**, 117; 1955, **32**, 179). It was also reported that the compound on selenium dehydrogenation formed a mixture of polyalkyl naphthalene derivatives.

The complete formulation of this non-bitter principle could not be worked out earlier because of the difficulties of assessing its correct molecular weight. The latter determined by Rast, by Beckmann's method or by titration was not satisfactory. The molecular weight has now been determined by X-ray analysis which indicates it to be 565. On the basis of this datum the formula of swietenine appears as $C_{32}H_{42}O_9$. The methoxyl function is now found to be associated with a methoxycarbonyl. A careful inspection of the infrared spectrum of the non-bitter principle in Nujol (peaks at 1506, 1030 and 877 $cm^{-1}$) and its UV spectrum (strong absorption near about 210 m$\mu$; $\epsilon$ nearly 32,000). suggests the presence of a furyl group, which also follows from the following evidences :

(*a*) The compound develops a pink coloration with hydrochloric acid and *p*-dimethylaminobenzaldehyde (Ehrlich's reagent). This is indicative of the presence of a $\beta$-substituted furan in the compound.

(*b*) During ozonolysis, swietenine generates formic acid like columbin (Barton and Elad, *J. Chem. Soc.*, 1956, 2085) (characterised as its *p*-phenylphenacyl ester, m.p. 84°). The other product of ozonolysis lacks the infrared frequency which corresponds to that of a furan ring (peaks at 1506, 1030 and 877 $cm^{-1}$ in Nujol).

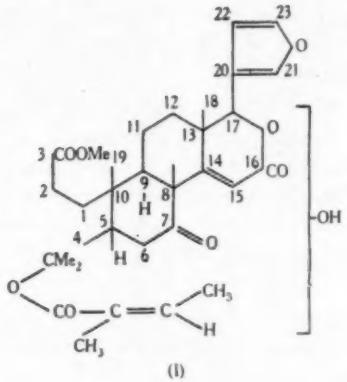
(*c*) Proton magnetic resonance spectrum (Corey *et al.*, *J. Amer. Chem. Soc.*, 1958, **80**, 1024) shows proton resonance at—113 and—62 cps, these n.m.r. signals being characteristic of a $\beta$-monosubstituted furan.

The compound has been further shown to be an ester of tiglic acid which is liberated during caustic potash fusion at 258°, as also during hydrolysis under mild conditions.

Swietenine contains five $-\overset{|}{\underset{|}{C}}.CH_3$ groupings and does not react with lead tetra-acetate, thus showing that the ketonic and tertiary hydroxyl groups are not vicinal. It does neither consume periodic acid showing the absence of an isolated double bond (Chatterjee *et al.*, *Anal. Chem.*, 1956, **28**, 878) in the compound.

The bicarbocyclic structure of swietenine (both the rings being six-membered) follows from the fact that the compound produces 1:2:5-trimethylnaphthalene (m.p. of trinitrobenzol adduct and its mixed m.p. with an authentic specimen being 153-54°) besides an *iso*propyl polyalkylnaphthalene derivative, $C_{16}H_{20}$, during selenium dehydrogenation (Chakrabartty and Chatterjee, this *Journal*, 1957, **34**, 117).

Based on these facts and on biogenesis of terpenoids as also from the strong analogy of swietenine with limonin (Arigoni *et al.*, *Exper.*, 1960, **16**, 41), coupled with the knowledge of the functional groups, the constitution (I) can be considered for swietenine.




(I)

(I)

Further work in confirmation of this structure is under way.

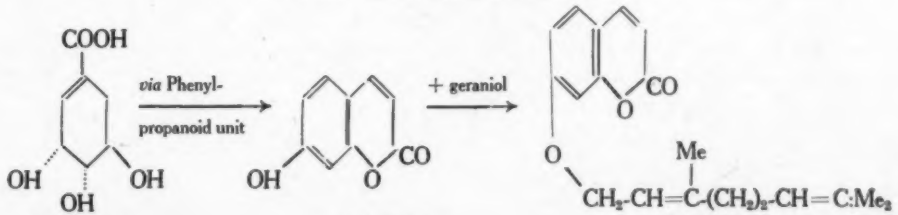
The authors wish to express their grateful thanks to the Govt. of W. Bengal for financial assistance in this work, and to the Varian Associates, California, for proton magnetic resonance spectra.

Department of Organic Chemistry,
University College of Science,
Calcutta-9.

*Received March* 14, 1960

**ERRATA**

Page 335. Read Structures (I) II) and (III) as :




Shikimic acid. (I)

Umbelliferone. (II)

Auraptene. (III)

[Jour. Indian Chem. Soc., Vol. 37, No. 7, 1960]

# SPOT TEST FOR IRON BY SUBSTITUTED VIOLURIC ACIDS

By R. P. Singh

Ferrous salts form deep blue complexes with numerous *iso*nitroso compounds. Although the reactions are extremely sensitive, these have rarely been used in analytical practice. Krohnke (*Ber.*, 1927, **60B,** 527; *Gas-wasserfach*, 1927, **70,** 510) used a chloroform solution of *iso*nitrosoacetophenone to detect as small as 0.03 mg. of iron per litre. Kuster (*Z. physiol. Chem.*, 1926, **155,** 157) found that a 0.0075% solution of ferrous sulphate showed a distinct reaction with *iso*nitrosoacetylacetone. Dubsky and Kuras (*Chem. Listy*, 1929, **23,** 496) have used diisonitroacetone for testing iron in the ferrous state.

During the course of investigations on the inner-complex salts of substituted violuric acids, the author (*Proc. Ind. Acad. Sci.*, 1946, **23A,** 330; *J. Sci. Ind. Res.*, 1956, **15B,** 245; this *Journal*, 1959, **36,** 198) found that all of them developed intense blue colour with iron in the ferrous state. Thiovioluric acids are better suited for this purpose because of their complexes being deeper in colour. Diphenyl-di-*o*-tolyl- and -di-*p*-tolyl-thiovioluric acids have been used for performing spot tests for iron.

*Procedure.*—A drop of a ferrous salt of iron is placed on a filter paper (Whatman No. 1) or a spot plate, followed by a drop of sodium acetate-acetic acid buffer (*p*H about 4.5). On adding a drop of an acetone solution of one of the violuric acids (0.5%), a deep blue colour is formed. To ensure the presence of iron in the ferrous state, the solution is first reduced with a small quantity of hydroquinone before addition of the reagent solution. An excess of hydroquinone does not interfere with the colour reaction.

*Sensitivity.*—This test can be used to detect as little as 0.1$\gamma$ iron on paper and 0.05$\gamma$ iron on a spot plate.

*Dilution limit* : 1:500,000 (on paper) and 1:1,000,000 (on a spot plate).

*Effect of pH.*—*p*H has a marked effect on the formation of the blue complex of iron (II) and must be within 3.1 and 6.0. *p*H adjustment can be done by addition of a drop of sodium acetate-acetic acid buffer.

*Effect of cations and anions.*—None of the common anions, such as, chloride, bromide, iodide, nitrate, nitrite, sulphate and thiocyanate or any of the common cations, were found to interfere in the detection of iron. Although complexes are formed with most other cations, but these do not interfere provided that their concentration does not exceed one part in 100,000. None of the common cations develop any appreciable colour at such high dilutions even though their relative proportions be 10 times that of iron. Iron, however, can be conveniently tested under these conditions. It has been found that oxalate, tartrate, citrate and cyanide ions interfere with colour development and should be absent.

Department of Chemistry,
University of Delhi,
Delhi-8.

*Received February* 13, 1960.

## *For Laboratory Reagent Quality Acids*

**To Precise Specifications**

| Maximum Limits of Impurities : | **Acid Sulphuric** $H_2SO_4$ : 98% w/w Sp. gr. 1.840 at 15°. | **Acid Nitric** $HNO_3$ : 69.8% w/w Sp. gr. 1.420 at 15°. | **Acid Hydrochloric** HCl:35.4% w/w Sp. gr. 1.180 at 15°. |
|---|---|---|---|
| Non-Volatile Matter : | 0.0025% | 0.01% | 0.001% |
| Chloride (Cl) : | 0.0002% | 0.00007% | — |
| Free Chlorine (Cl) : | — | — | 0.0002% |
| Nitrate ($NO_3$) : | 0.00002% | — | — |
| Sulphate ($SO_4$) : | — | 0.0003% | 0.0003% |
| Heavy Metals (Pb) : | 0.0002% | 0.0002% | 0.0002% |
| Iron (Fe) : | 0.0001% | 0.0001% | 0.0001% |
| Arsenic (As) : | 0.1 part per million | 0.02 part per million | 0.04 part per million |
| Ammonium ($NH_4$) : | 0.0005% | — | — |
| Selenium (Se) : | 0.001% | — | — |
| Oxygen Absorbed (O) : | 0.00015% | — | — |

**We invite orders and enquiries.**

**Write us about your requirements**

**for other reagent quality chemicals.**

## Bengal Chemical & Pharmaceutical Works, Ltd.

CALCUTTA :: BOMBAY :: KANPUR

Office : 6, Ganesh Chunder Avenue, Calcutta-13

Gram : LILICOM CALCUTTA Phone : 23-1316

**LILICO PRIVATE LIMITED.**

3, MANGOE LANE, CALCUTTA-1

*DISTRIBUTORS OF*

**WHATMAN FILTER PAPERS**

**FINE CHEMICALS**

FOR ANALYTICAL, PHARMACEUTICAL, PHOTOGRAPHIC, RESEARCH AND TECHNICAL PURPOSES

**STANDARD STAINS AND INDICATORS : PRODUCTS OF M/S. HOPKIN & WILLIAMS LTD. & L. LIGHT & CO., LTD.**

**AVOSET SUGAR OF MILK (U.S.A.)**

*IMPORTERS & DEALERS IN*

FILTER PAPERS, CHEMICALS, LABORATORY REQUISITES, APPARATUS ETC.

*Enquiries Solicited from*

IMPORTERS, DEALERS & USERS

GS Gas PLANTS

*FOR*

**HEATING**

IN

LABORATORY

INDUSTRY

KITCHEN

**GANSONS**

**PRIVATE LIMITED.**

**P.O.B. 5576, BOMBAY-14.**

**—Also makers of—**

Superior Laboratory Fittings

Atomic Equipments.

Sigcol

LABORATORY GLASS APPARATUS

●

*Sole Selling Agents :*

**GHARPURE & CO.**

**P-36, ROYAL EXCHANGE PLACE EXTN. CALCUTTA-1**

Gram : MEENAMO. Phone : 22-2061

BOROSIL

LABORATORY GLASSWARE

*such as*

FLASKS, BEAKERS, CONDENSERS, MEASURING FLASKS, MEASURING CYLINDERS, PIPETTES & ANY SPECIAL APPARATUS MADE TO DESIGN

*and*

PENICILLIN VIALS, VACCINE BULBS—WHITE & AMBER

ALL OTHER APPARATUS & EQUIPMENT MANUFACTURED TO CLIENT'S DESIGN

**INDUSTRIAL & ENGINEERING APPARATUS CO. PRIVATE LTD.**

**CHOTANI ESTATES, PROCTOR ROAD GRANT ROAD, BOMBAY 7.**

Phone : 34-3176. Telegrams : Nadiachemi.

# NADIA CHEMICAL WORKS PRIVATE LTD.

C 44, 45 & 46, COLLEGE STREET MARKET, CALCUTTA-12.

*Manufacturers of :-*

1. *CHEMICALS*—Benzene, Toluene, etc., Bromine, Halogen derivatives of both Organic and Inorganic compounds and other fine Laboratory Chemicals

2. STILLS for distilling Essential Oils, Alcohols, Water, etc.
   RECTIFIERS, CONDENSERS, etc.

3. OVENS, Baths, etc. for Gas, Oil or Electric heatings.

4. Scientific Apparatus (PHYSICAL, CHEMICAL, BIOLOGICAL, etc.) of both Glass and Metal.

5. MICRO-ANALYSIS APPARATUS.

*Please ask for Estimates.*

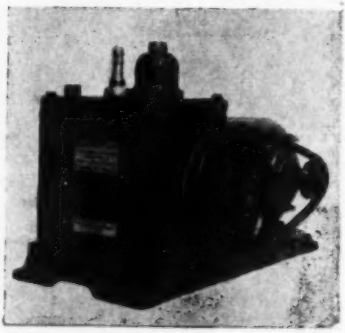
VERY RELIABLE INDIGENOUS SUBSTITUTES
OF GUARANTEED ANALYTICAL REAGENTS
MAY BE FOUND IN

"BASYNTH"
Brand
ANALYTICAL REAGENT

Acid Hydrochloric
Acid Hydrochloric Fuming
Acid Sulphuric
Acid Nitric
Acid Nitric Fuming
Acid Acetic Glacial
Ammonium Hydroxide
Benzene
Toluene
Xylene
Petroleum Ether
Amyl Alcohol
Butyl Alcohol Etc., Etc.

BASIC & SYNTHETIC CHEMICALS, PRIVATE LTD.
P. O. Jadavpur College, Calcutta-32

MADE IN INDIA
HIGH VACUUM ROTARY PUMP
Single Stage & Two Stage
With or Without Air Ballast
*All Indian Materials and Construction*



BASIC & SYNTHETIC CHEMICALS PRIVATE LIMITED
P. O. Jadavpur University, Calcutta-32

* FOR YOUR REQUIREMENTS
OF ALL KINDS OF EQUIPMENTS FOR RESEARCH *

RAJ-DER-KAR & CO.,

SADHANA RAYON HOUSE, Dr. D. NAOROJI ROAD, BOMBAY-1

Branch Office :
44/6, Regal Building, Connaught Place, New Delhi.

TELEPHONE : 26-2304
TELEGRAM : TECHLAB

*A few of our Agencies :*

* LUDWIG SEIBOLD, Austria,
For *p*H Testers, Titrators
and Recorders, etc.

EASTMAN KODAK, U. S. A.,
For All Sorts of Complex
Organic Chemicals.

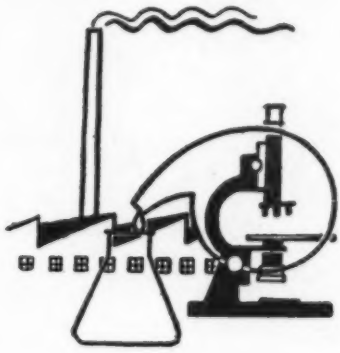
* W. A. TAYLOR & CO., U. S. A.,
For *p*H Comparators, Indicators,
Water Analysers, etc.

* TRACERLAB Inc., U. S. A.,
For Radiochemicals & Equipments
for Nuclear Research.

# We Manufacture..

*Laboratory Chemicals & Reagents*

**of a wide range under rigid control and expert supervision to ensure guaranteed standard & reliability.**



## A selection from our range :

*Acetone
*Alcohol Methyl
*Barium Carbonate
*Barium Chloride
*Benedicts' Solution
*Benzene
*Carbon Tetrachloride
*Lead Acetate
*Liquor Ammon Fort
*Magnesium Sulphate XL
*Xylol

**THE CALCUTTA CHEMICAL CO., LTD.**

**HEAD OFFICE: 35, PANDITIA ROAD, CALCUTTA 29.**

*Branch Office & Depots at :*

**Delhi, Madras, Bombay, Bangalore, Vizag, Ranchi, Nagpur, Jamshedpur, Patna, Bilaspur, Bhagalpur, Madhupur, Asansol, Siliguri.**

*A Monumental Work* *Published March 1959*

**A book that should find place on the shelves of every Library**

# HISTORY OF CHEMISTRY IN ANCIENT & MEDIEVAL INDIA

*Incorporating*

**HISTORY OF HINDU CHEMISTRY**

**by Acharya Prafulla Chandra Ray**

*Edited by* Prof. P. Rây

Royal 8*vo*. Rexin bound, 494 pages with 39 illustrations.

Price *ex*-postage : Prime Edition : —Rs. 24/- (Inland), Ordinary Edition —Rs. 20/- (Inland)
£ 2/- or $ 6.00 (Foreign)

For Fellows ,, ,, Rs. 20/- ,, ,, Rs. 16/-

An invaluable book for students of science and history and to all persons interested in the scientific heritage of India.

PUBLISHED BY THE INDIAN CHEMICAL SOCIETY

**92, Acharya Prafulla Chandra Road, Calcutta-9, INDIA.**

**Some Opinions :**

*Nature, January 5, 1957.*

" Since there is much new material in the book, all those who are fortunate enough to have the earlier edition will wish to have the new one.

All those interested in the History of Chemistry owe a debt of gratitude to Prof. P. Rây and the Indian Chemical Society for its publication ".

J. R. Partington.

*Journal of Chemical Education, February, 1957 :*

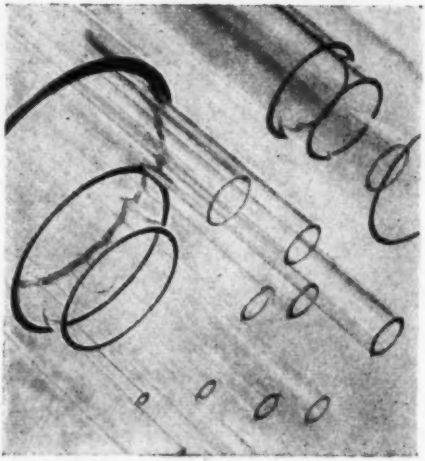
".....Professor Rây, in his carefully constructed revision of Prafulla Chandra Ray's standard 'History of Hindu Chemistry' has given us a highly informative and interesting description of Indian Chemistry. In chronological order, the contributions of Indians to chemistry have been recorded from the Harappa period of the fourth millennium B.C. to the end of Mogul culture.....Many of the ideas described make delightful reading for the average chemist with a historical bent.....chemists and historians of chemistry will find in this book a valuable assessment of ancient Indian chemistry and culture".

*ISIS-Vol. 49, p. 362, Sept., 1958.*

".....this new book is very valuable both as a re-edition of an out-of-print classic collection of fundamental data and as a presentation of much well illustrated documentation of Indian achievements in the practical arts in the field of chemistry, according to the archæological findings ".

J. Filliozat.

# Through thick and thin Pyrex



Everyone who makes glass apparatus needs Pyrex Tubing. The Pyrex catalogue lists no fewer than 80 standard lines, all in healthy demand. Who uses all this tubing? Hospitals, research labs for Government and industry, universities, schools. PYREX are always improving their production methods to attain even higher standards of quality. This is one good reason (among many) why everyone who is looking for quality glassware looks for PYREX

## Pyrex tubing

is made from Pyrex borosilicate glass

It is therefore
heat-resistant
mechanically strong
chemically durable
—and functionally matches all other PYREX glass apparatus

In addition, its chemical composition is now completely free from arsenic

**Sizes** 2 mm to 100 mm o/diam—the largest size-range available in borosilicate glass

**Wall Thickness** Standard Wall, Heavy Wall, Extra Heavy. Also Capillary range

**Length** Tubing is supplied in standard lengths of approximately 5 feet

**SPECIAL** problems concerning manipulated tubing can be referred to the PYREX Service Department, who will gladly construct special laboratory equipment to your drawings, in consultation (if necessary) with your scientific and technical staff

**PYREX**

*Regd. Trade Mark*

MADE IN ENGLAND PYREX

## Laboratory and scientific glass

*AVAILABLE FROM ALL LEADING DISTRIBUTORS*

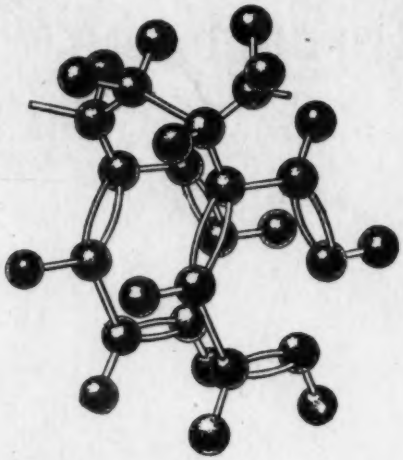
*SOLE AGENTS:*

GORDHANDAS DESAI PRIVATE LTD.

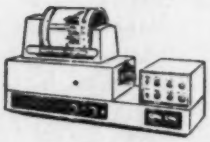
PHEROZESHAH MEHTA ROAD, FORT, BOMBAY-1

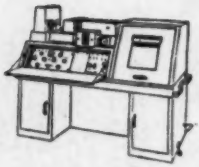
Also at CALCUTTA, MADRAS & NEW DELHI

# ANALYTICAL INSTRUMENTS by Perkin-Elmer



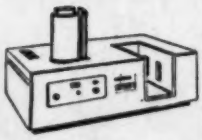
**MODEL 221 DOUBLE BEAM RECORDING INFRARED SPECTROPHOTOMETER**
The most refined instrument for infrared analysis

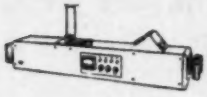




**MODEL 13-U UNIVERSAL SPECTROPHOTOMETER**
A highly flexible instrument covering complete ultraviolet, visible and infrared regions

**MODEL 137 INFRACORD DOUBLE BEAM SPECTROPHOTOMETER**
A new instrument for routine infrared analysis

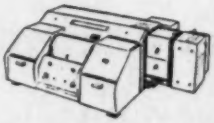


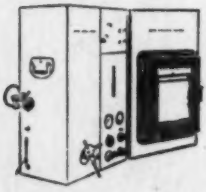


**MODEL 38-A ELECTROPHORESIS APPARATUS**
For analysis and separation of complex solutions

**MODEL 146 FLAME PHOTOMETER**
For rapid analysis of any element in solution with visible emission lines

**SPECTRACORD MODEL 400OA RECORDING SPECTROPHOTOMETER**
For ultraviolet, visual, near infrared regions. Features double monochromator





**MODEL 154-C VAPOR FRACTOMETER**
A new, low cost gas chromatography apparatus for analysis of gases and liquids boiling upto 325°C

PSBS-24/59

P E C

Perkin-Elmer is proud to present a complete line of analytical instruments for the spectroscopic or chemical laboratory. Each embodies the most recent technical advances in its particular field—each is constructed with Perkin-Elmer's characteristically high standard of quality and workmanship, and each is backed with a complete set of accessories to make it useful for the widest possible range of problems.

The variety of instruments now available from Perkin-Elmer permits the equipping of a laboratory for practically all types of analyses with instruments of a single manufacturer. This can result in considerable savings in servicing, and in inventories of accessories.

*Sold and serviced in India exclusively by*

**BLUE STAR**

**BLUE STAR ENGINEERING CO. (Calcutta) Private LTD.**
7 HARE STREET, CALCUTTA 1
Also at BOMBAY · DELHI · MADRAS

**PRESIDENT :**

K. VENKATARAMAN, D.Sc., F.N.I.

**VICE-PRESIDENTS :**

(who have filled the office of President)

P. K. BOSE, D.Sc., F.N.I.
N. R. DHAR, D.Sc., DR.ES. Sc., F.R.I.C., F.N.I.
B. C. GUHA, D.Sc., PH.D., F.N.I.
P. C. GUHA, D.Sc., F.N.I.
J. N. MUKHERJEE, C.B.E., D.Sc., F.A.S.B., F.N.I.
MATA PRASAD, D.Sc., F.R.I.C., F.N.I.
J. N. RAY, O.B.E., D.Sc., F.R.I.C., F.N.I.
P. RAY, M.A., F.N.I.

**VICE-PRESIDENTS :**

B. N. GHOSH, D.Sc., F.N.I.
P. B. SARKAR, DR.ES.Sc., F.N.I.
V. SUBRAHMANYAN, D.Sc., F.R.I.C., F.N.I.
V. M. BHAVE, M.Sc., Ph.D., A.R.I.C.
President of Bombay Branch *(ex-officio)*.

**HONY. SECRETARY :**

M. M. CHAKRABARTY, M.Sc., PH.D.

**HONY. TREASURER :**

D. CHAKRAVARTI, D.Sc., F.N.I.

**MEMBERS OF THE COUNCIL :**

J. C. BARDHAN, D.Sc.
A. K. BHATTACHARYA, D.Sc., F.R.I.C.
MRS. ASHIMA CHATTERJEE, D.Sc.
B. CHATTERJEE, D.Sc., F.N.I.
A. C. CHATTERJI, D.Sc., DR. ING.
R. D. DESAI, D.Sc., F.R.I.C., F.I.I.Sc., F.A.Sc., F.N.I.
K. S. G. DOSS, D.Sc., F.N.I., F.R.I.C., F.INST.P.
M. O. FAROOQ, M.Sc., PH.D.
T. N. GHOSH, D.Sc., F.N.I.
J. GUPTA, D.Sc.
S. M. MEHTA, B.A., M.Sc., F.A.Sc., A.R.I.C., F.N.I.
T. N. MEHTA, M.Sc., PH.D.
R. P. MITRA, D.Sc., F.N.I.
S. N. MUKHERJEE, D.Sc.
P. V. NAIR, M.Sc., D.PHIL.
B. PRASAD, D.Sc., F.N.I.
T. R. SESHADRI, M.A., PH.D., F.R.S.
R. C. SHAH, M.Sc., PH.D., F.N.I., F.R.I.C.
B. S. SRIKANTAN, D.Sc.
S. H. ZAHEER, M.A., PH.D.

**HONY. EDITORS :**

D. K. BANERJEE, D.Sc.
A. N. KAPPANNA, D.Sc.

**BOARD OF ASSOCIATE EDITORS :**

U. P. BASU, D.Sc., F.N.I.
MRS. A. CHATTERJEE, D.Sc.
B. CHATTERJEE, D.Sc., F.N.I.
P. C. DUTTA, D.Sc.
B. C. GUHA, D.Sc., PH.D., F.N.I.
S. S. JOSHI, D.Sc., F.N.I.
R. P. MITRA, D.Sc., F.N.I.
S. M. MUKHERJI, D.Sc., F.N.I.
S. N. MUKHERJEE, D.Sc.
P. RAY, M.A., F.N.I.
S. P. RAYCHAUDHURI, D.Sc., PH.D., F.N.I., F.R.I.C.
P. B. SARKAR, DR.ES. Sc., F.N.I.
R. C. SHAH, M.Sc., PH.D., F.N.I., F.R.I.C.
S. H. ZAHEER, M.A., PH.D.

**HONY. AUDITORS :**

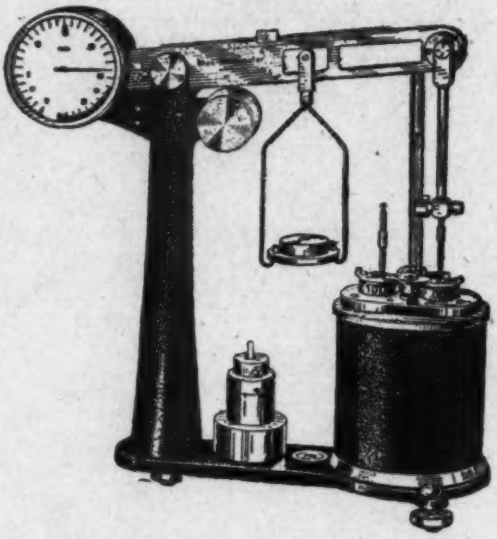
P. C. NANDI, M.A., B.Sc., A.C.A.R.A.
A. B. GUPTA, B.Sc., L.L.B., A.C.A.R.A.

ASST. SECRETARY :
K. L. MUKHERJEE, M.Sc.

ASST. EDITOR :
G. BANERJEE, M.Sc.

Regtd. No. C 1878


# HOPPLER RHEO-VISCOMETER



AN ABSOLUTE VISCOMETER

FOR

VISCOSITY MEASUREMENTS OF
HIGH FLUID SUBSTANCES,
HIGHLY VISCOUS EMULSIONS,
PASTES, FATS, ETC.

•

Measuring Range: 0.5 to 1000000 C

Accuracy: ± 0.5%

Temparature Range:—60° to + 120°C

*Manufactured by:*

VEB PRUFGERATE-WERK, MEDINGEN

DRESDEN—GERMANY.

*Sole Agents in India:*

GORDHANDAS DESAI PRIVATE LIMITED

SIR PHEROZESHAH MEHTA ROAD, BOMBAY-1

*Branches:*

P-7, Mission Row Extension
CALCUTTA-1

4/2B, Asaf Ali Road
NEW DELHI

22, Linghi Chetty Street
MADRAS-1


Published by G. Banerjee, M.Sc., Asst. Editor, Indian Chemical Society, 92, Acharya Prafulla Chandra Road, Calcutta-9 and Printed by D. A. Lakin at The Statesman Press, Chowringhee Square, Calcutta-1.